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THE PYROLYSIS OF ALBERTA NATURAL GAS

by

PAUL E. GISHLER

Department of Chemistry,
niversity of Alberta,
ril, 1931.

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THESIS

THE PYROLYSIS OF ALBERTA NATURAL GAS

by

P. E. GISHLER

Submitted in fulfilment of the
requirement for the degree of
Master of Science.

UNDER THE DIRECTION OF

Dr. E. H. BOOMER

APRIL, 1931.

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THE PYROLYSIS OF ALBERTA NATURAL GAS

I - INTRODUCTION

Of the natural resources of the province of Alberta, the gas fields occupy a position second only to the coal measures. In general, the gas fields may be classified as "wet" or "dry". Examples of the latter are to be found at Viking in the North, and at Bow Island or Foremost in the South. Of "wet" gas fields there is at present only one - the Turner Valley field. The dry gas fields are under control and are used as needed to furnish industrial and household fuel. The Turner Valley field differs in this respect, being exploited primarily for the naphtha content of the gas issuing from the wells. Little or no account has been taken in the past of the gas, and the larger part of it has been destroyed by burning in the open air at the field. A small part is treated for hydrogen sulfide removal and is used in the City of Calgary or in the field as fuel.

The magnitude of the waste cannot be estimated with precision because of the lack of control of any sort over the field. In 1926 reliable estimates placed the waste in the neighborhood of 250 million cubic feet per day, and at the present time competent observers estimate it to be not less than 400 million cubic feet. Various figures, as high as 600 million feet, have been suggested.

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The quantity used in the neighboring city amounts to some 75 million cubic feet.

With no immediate prospect of a market sufficient to absorb this gas as a fuel in sight, and in view of the obvious difficulties of shutting down a field containing much invested capital, an investigation of natural gas as the raw material of chemical processes was undertaken. The present investigation deals with one phase of the subject; namely, the thermal treatment of natural gas in such a manner that the saturated gaseous hydrocarbon constituents are converted partly to other gaseous products and partly to liquid and solid hydrocarbons.

Gases from both the dry field at Viking and the "wet" field in Turner Valley have been examined. There is considerable difference in the composition of these two gases.

The Viking gas is largely methane. Distillation analysis shows it to contain#

methane	95.7	%
ethane	1.4	
propane	0.9	
nitrogen	2.0	

The Turner Valley gas is of interest only after its naphtha content has been removed. The naphtha is removed by suddenly expanding the gas from the well at approximately 1000 to 350 pounds per square inch. The process of liquifying and collecting the naphtha takes place in

---

(# The above analysis has been obtained through the courtesy of the Mines Branch)

Smith Separators. The waste gas leaving these separators has the following composition on the average:

methane	88.5 %
ethane	6.5
propane	3.3
butane & higher	0.5

The sulfur exists in the form of hydrogen sulfide and mercaptans. The amount of these sulfides is found to vary from 0.5 to 2.0% of the gas by volume. The sulfur compounds are removed in part from the gas which is to be used as fuel.

In part of the work on Turner Valley gas sulfur free gas was used and in the remaining work the "unscrubbed" gas was used.

The subject of investigation may be divided into two major and several minor parts as indicated below:

1. Work on Viking Gas.
    a. Using quartz reaction tubes, to determine the maximum oil yields throughout the temperature range in which oils are produced by pyrolysis.
    b. To investigate the possibility of pyrolysis in steps.
    c. To study the effect of the surface of the reaction tube on yield.
2. Work on Turner Valley Gas.
    a. To investigate the temperature range most suitable for oil production and to determine the yields

throughout this temperature range.

b. To determine what effect pyrolysis in steps has on the yield and on the nature of oil products.

In addition, the development of the methods of operation, recovery of products, and analysis is presented. Considerable experience has shown the immense importance of the methods of collection and the temperature measurement.

A discussion of the proposed mechanism of the reaction is presented in the review of the literature and this question receives consideration in the light of the present results.

II - LITERATURE REVIEW

In 1825 Faraday (11) decomposed aliphatic oil and noted the formation of aromatic products. Since then many workers have studied the effect of heat treatment on aliphatic hydrocarbons in an endeavor to determine either the mechanism of the reaction or the yield of oil products. The work has been either on pure hydrocarbons such as methane, ethane, etc., or on mixtures of these such as are found in natural gas.

Natural gas usually consists of varying mixtures of the low boiling straight-chained saturated hydrocarbons. These on thermal treatment yield a variety of products both aliphatic and aromatic. Methane, the simplest hydrocarbon, on decomposing, yields varying amounts of acetylene, ethylene, ethane, butadiene, etc., besides benzene, homologues of benzene, and condensed ring aromatics. A study of the behavior of these substances at high temperatures is necessary in order to understand the reactions involved in going from aliphatic hydrocarbons to benzene and tar.

Berthelot (3) was the first to attempt to solve the mechanism involved in the decomposition of methane. He concluded that direct decomposition to carbon and hydrogen does not take place, but that two or more molecules combined to form a heavier hydrocarbon with less hydrogen.

This polymerization continued until the final end products, carbon and hydrogen, were obtained. The mechanism of decomposition which Berthelot proposed may be condensed into the following diagram:

$$\begin{tikzcd} 4CH_4 \arrow[r, leftrightharpoons] & 2C_2H_6 + 2H_2 \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons] & 2CH_4 + C_2H_2 + 3H_2 \\ & 2C_2H_4 + 4H_2 \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons] & C_2H_6 + C_2H_2 + 4H_2 \\ & 2C_2H_2 + 6H_2 & \end{tikzcd}$$

$$3\,C_2H_2 \rightarrow C_6H_6 \longrightarrow \text{Complex tars;} \quad \text{C and H}$$

He stressed the formation of acetylene, which he believed polymerized to form aromatic products.

Bone and Coward (4) studied both methane and ethane. They found methane to be much more stable than ethane. The decomposition of ethane occurred throughout the body of the gas whereas they found that the decomposition of methane was a surface phenomenon. Bone and Coward detected acetylene only in traces and concluded that it does not play any important part in the formation of aromatic hydrocarbons.

They found that ethane decomposes in the following manner at 675°C.

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \longrightarrow C + CH_4 + H_2$$

This was explained by assuming the formation of $\cdot CH_3$, $:CH_2$ and $\vdots CH$ groups. These highly unstable residues in the absence of hydrogen would tend to decompose to carbon and hydrogen. In the presence of a large amount of hydrogen, hydrogenation would take place to form methane.

To prove this point they ran comparative experiments using ethane plus hydrogen in the one case and ethane plus nitrogen in the other. In the presence of an excess of hydrogen there was a large increase in methane formation, thus justifying the claim for the presence of the above-mentioned unstable groups.

Williams Gardner (30) studied ethane more intensively between the temperatures 500 and 900°C. and arrived at a more detailed mechanism than that of Bone and Coward. This mechanism is more or less self-explanatory and is given below:

$$C_2H_6 \xrightleftharpoons{550^\circ C} 2\cdot CH_3 \xrightleftharpoons{600^\circ C} 2:CH_2 + \cancel{CH} + H_2 \xrightleftharpoons{550-700} C_2H_4$$

Hydrogenation at all temperatures.

$$2\cdot CH_3 + H_2 \rightarrow 2\ CH_4$$

$$:CH_2 + H_2 \rightarrow CH_4$$

Dehydrogenation 650 - 850°C.

$$2\cdot CH_3 \rightleftharpoons 2:CH_2 + H_2$$

$$:CH_2 \rightarrow C + H_2$$

$$2\cdot CH_3 \rightarrow 2\ C + 3H_2$$

Polymerization 700 - 850°C.

$$n:CH \rightarrow C_n\ H_n$$

$$n:CH \rightarrow C_n\ H_{n-m} + \frac{m}{2}H_2$$

It was Davidson (9), working on the ethane-propane fraction of natural gas, who first noted the formation of butadiene when ethane decomposed. A small percentage of aromatic hydrocarbons was also found. Davidson proposed the ethane to ethylene to butadiene to benzene mechanism which is represented below:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$H_2C:CH_2 + H_2C:CH_2 \rightarrow H_2C:CH \cdot HC:CH_2 + H_2$$

$$H_2C:CH \cdot HC:CH_2 + H_2C:CH_2 \rightarrow C_6H_6 + 2H_2$$

Hague and Wheeler (15) have studied the simple aliphatic hydrocarbons in an endeavor to solve the mechanism of aromatic formation. They attacked the problem by making a quantitative analysis of the products formed on pyrolysis and finding the relations between yields and percentages of gaseous products. In their work on propane they found that 69% decomposed to form ethylene and hydrogen, while the remaining 31% formed propylene and hydrogen.

Frey and Smith (13) arrived at similar conclusions.

Hurd and Spence (18) studied butane at 600 and 700°C. At 600°C. they found that the two following equations accounted for its decomposition:

1. $C_4H_{10} \rightarrow CH_4 + C_3H_6$
2. $C_4H_{10} \rightarrow C_2H_6 + C_2H_4$

At 700°C. the four following equations are given, along with the extent of each decomposition in percent.

1. $C_4H_{10} \rightarrow C_2H_6 + C_2H_4$ 46%
2. $C_4H_{10} \rightarrow CH_4 + C_3H_6$ 44%
3. $C_4H_{10} \rightarrow H_2 + C_4H_8$ 5%
4. $C_4H_{10} \rightarrow 2H_2 + C_4H_6$ 4%

Hague and Wheeler explain the decompositions of butane at 650°C. by the following three equations:

1. $C_4H_{10} \rightarrow C_2H_6 + C_2H_4$ 43%
2. $C_4H_{10} \rightarrow CH_4 + C_3H_6$ 36%
3. $C_4H_{10} \rightarrow H_2 + C_4H_8$ 21%

The above equations do not include the formation of butadiene, whereas Hurd and Spence, at 700°C, found 4%.

There are at present two explanations worthy of consideration for the formation of aromatic hydrocarbons by the pyrolysis of simple aliphatic hydrocarbons. The one has been developed by Stanley and Nash (26), who have enlarged on the assumptions of Bone and Coward (4) of unstable $\cdot CH_3$, $:CH_2$, and $\vdots CH$ groups. These are considered to combine in various ways, as described previously in the work by Williams Gardner, to form higher aliphatic and aromatic compounds. The other explanation, as developed by Hague and Wheeler, enlarges on the findings of Davidson, who used the steps ethylene to butadiene to benzene.

Stanley and Nash assume that the unstable intermediate residues, as propounded by Bone and Coward, may either polymerize or break down to carbon and hydrogen, depending on such conditions as temperature, pressure and duration of heating. Polymerization will lead to the formation of ethane, ethylene and acetylene. Very little ethane will be formed at high temperatures due to its instability. The important step in this mechanism is the formation of $:CH_2$ groups which lose a hydrogen atom to form $:CH$ groups. It is these groups which are responsible for the formation of liquid products.

Stanley and Nash are doing further work on the mechanism and at present propose the following provisional scheme:

$$\begin{tikzcd}
 & 2\ CH_4 \arrow[d] \\
C_2H_6 \arrow[r, phantom, "\rightleftharpoons"] & 2\cdot CH_3 + H_2 \arrow[d] \\
C_2H_4 \arrow[r, phantom, "\rightleftharpoons"] & 2:CH_2 + H_2 \arrow[d] \\
C_2H_2 \arrow[r, phantom, "\rightleftharpoons"] & 2:CH + H_2 \arrow[d] \\
 & 2\ C + H_2
\end{tikzcd}$$

$$n\ :CH \longrightarrow C_n H_n$$

$$n\ :CH \longrightarrow C_n H_{n-m} + \frac{m}{2} H_2$$

Hague and Wheeler (15), after an extensive study of the straight-chained aliphatic hydrocarbons up to and including hexane, come to definite conclusions. These investigators find that below 750°C. each hydrocarbon has

its own peculiar mode of decomposition, but at higher temperatures they all behave similarly. With the exception of methane they decompose to yield a maximum of ethylene at 700-750°C. Wheeler and Wood found that under similar conditions these hydrocarbons all yielded the same kind of liquid products; namely, aromatics. This indicates that the common source of the aromatics is in the C_2 unsaturated hydrocarbons, and acetylene need not be postulated as responsible for the formation of aromatics. Hague and Wheeler claim that ethylene alone is responsible for the aromatic hydrocarbons found. Ethylene is fairly stable up to 750°C. and will yield aromatic compounds at 700°C. At higher temperatures it was found that the percentage of aromatic oil was proportional to the amount of ethylene in the residual gas.

With ethane, propane, butane and pentane, the maximum percentage of ethylene in the residual gas was 24, while for each of the above gases the maximum yield of aromatic oil products was 24%. Hexane decomposed to yield 33.2% ethylene, and 33.8% oil was obtained.

According to Hague and Wheeler the mechanism commencing with ethylene may be represented as

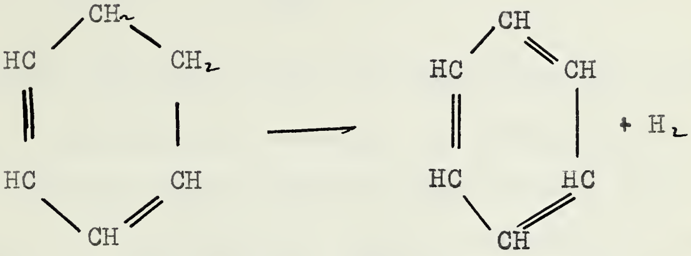
1. $CH_2:CH_2 + CH_2:CH_2 \longrightarrow CH_3 \cdot CH_2 \cdot CH:CH_2$

2. $CH_3 \cdot CH_2 \cdot CH:CH_2 \longrightarrow CH_2:CH \cdot CH:CH_2 + H_2$

3. $CH_2{:}CH{\cdot}CH{:}CH_2 + CH_2{:}CH_2$

(a) $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$

or (b) $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH + H_2$



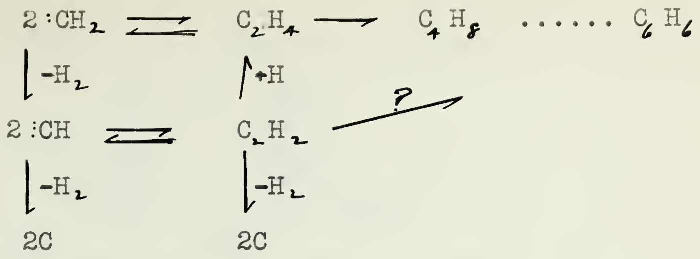
Methane cannot yield ethylene as a primary decomposition product, and yet it yields aromatic hydrocarbons on pyrolysis. Hague and Wheeler used the Bone and Coward unstable residues as the intermediate step in the formation of ethylene from methane. This may be expressed as

$$CH_3{\cdot}H \longrightarrow {:}CH_2 + H{\cdot}H$$

$$2\,{:}CH_2 \longrightarrow C_2H_4$$

In a more recent publication, Wheeler and Wood (29), although still assigning to ethylene the major role, stress the importance of ${\cdot}CH_3$, ${:}CH_2$, and ${\vdots}CH$ residues. They modify the Stanley and Nash mechanism to look like the following

$$\begin{tikzcd}
2\,CH_4 \arrow[d, "-H_2"] & \\
2{\cdot}CH_3 \arrow[r, shift left] \arrow[d, "-H_2"] & C_2H_6 \arrow[l, shift left] \arrow[d, "-H_2"] \\
{} & {}
\end{tikzcd}$$



It is not until quite recently that any study was made of the yields of aromatic oil obtainable from natural gas. Fischer (12) in 1928 studied various tubes and catalysts at temperatures ranging from 900 to 1200°C. It was found that light vapors were produced at 900°C., but the yield was low. A temperature of 1200°C. was too high as it tended to promote the reaction

$$CH_4 \longrightarrow C + 2H_2$$

The maximum yield was obtained at 1150°C. with a reaction time of 0.5 seconds in a quartz tube. The natural gas was chiefly methane and gave a 12.9% yield. Porcelain was found to produce lower yields than quartz, whereas iron, copper, potassium hydroxide and graphite promoted carbon and hydrogen formation. It was found that Al_4C_3 tended to increase the light oil to tar ratio. Inert gases were found to have no effect except that they necessitated a rise in temperature to produce the same corresponding yields.

An analysis of the tar produced by Fischer showed the following

I.B.P - 200° C.
14% - 250° C.
29% - 360° C.

Distillation of the light oil yielded

7.8% to 55°C.
61.1% - 85°C.
12.6% - 115°C.
3.9% - 145°C.
14.6% - over 145°C.

Wheeler and Wood (28) used a quartz tube and obtained a maximum yield at 1050°C. They did not work at higher temperatures. They also found quartz to give slightly higher yields than porcelain. Quartz tubes packed with broken quartz were compared with unpacked tubes, and no appreciable difference in the reaction was found. Horizontal tubes were found to give higher yields than vertical tubes, and contrary to Fischer's results, dilution with hydrogen was found to lower the yield.

Stanley and Nash (26) used a 5 mm. quartz tube at temperatures up to 1150°C. They obtained a yield of 11.0% oil. The maximum yield was found to correspond to a maximum in the acetylene and ethylene curves.

Chamberlain and Bloom (6) reported work on two different gases. One consisted almost entirely of methane, while the other contained 23% ethane. The work was done at 700 to 900°C. Practically no tar was obtained, and a yield of 8.4% benzene was reported. This result is definitely out of line with other work, and with the results of the recent work. An attempt to duplicate the results of Chamberlain and Bloom was made, but no equivalent results

could be obtained. Failure to do so must be attributed to a misinterpretation of their procedure, which is presented in this report in an ambiguous manner.

The higher straight chained aliphatic hydrocarbons have been found to produce larger yields of aromatic oil. Zanetti (31) in 1916, working on the propane butane fraction, obtained yields of tar as high as 16% by weight. The condenser system consisted of a Cottrell (8) unit only, and consequently considerable light oil would be lost and not included in the above figure. In a later paper Zanetti and Egloff (32) identified some of the constituents of the tar.

On fractionation they obtained

To 95°C.	4.8%
95 - 120	2.0%
120 - 150	3.9%
150 - 170	0.7%
To 170°C.	14.1%
170 - 230	13.6%
230 - 270	12.7%
270 - 365	16.3%
Pitch	43.3%

Benzene and toluene were identified by nitration. The picrate of naphthalene was formed. Acenaphthene was identified: (1) by crystallizing from alcohol.

(2) by forming the picrate.

Anthracene and phenanthene were separated and the picrate formed. Pyrene and Chrysene were also isolated and identified.

It has already been stated that yields of 24% were obtained from ethane, propane, butane and pentane. This refers to the work of Hague and Wheeler (15) who studied the above hydrocarbons between the temperatures of 600 and 1000°C.

A comprehensive review of the work up to 1916 is given by Lomax Dunstan and Thole (20). Egloff, Schaad and Lowry (10) have presented the work on the Pyrolysis of Hydrocarbons in detail. Work up to 1930 is included.

III - EXPERIMENTAL METHODS

A description of the experimental methods may be conveniently classified as follows:

1. The measurement and control of the rate of gas flow, and the total gas volume.
2. The measurement and control of the reaction temperatures and as a corollary the relation of temperature measurement to the true gas temperature.
3. The collection of the products of the reaction.
4. The analysis of these products.

Each of the above will be dismissed in turn. The first and fourth do not offer any difficulties and can be discussed with a brief description. The second and third sections will be treated in considerable detail. It is obvious that care must be taken in the temperature measurements for a variety of reasons; first the thermocouple could not be inserted in the gas stream itself; second, the temperature was not uniform over the reaction tube length, and lastly, the temperature of a stream of gas is not that of the walls of the container, nor is it that of a thermocouple inserted in the gas stream. In regard to collection of the products, the material dealt with is in the form of a dilute mixture of benzene and other vapors in a complex gas, and tar is produced in

the form of an exceedingly stable fog. Considerable development was necessary before a satisfactory method of quantitative recovery was obtained.

1 - Gas Control

The rate of flow of gas was measured by means of a capillary flow-metre. The flow-metre was of the type that allowed the ready replacement of the capillary tube. A number of capillaries of varying length and diameter were prepared and calibrated to cover a wide range of gas flow. Each capillary was calibrated by determining the time at various constant rates for the passage of a quantity of gas as measured by a wet test meter. The rate during an experiment was checked against the total volume as measured on a test meter and the time of the experiment. The flow-metre is shown in Plate II-A.

The total volume of gas used was measured by means of a Sargent Wet Test Metre filled with mineral seal oil. The gas metre was carefully calibrated by comparison with a calibrated gas holder. Oil was added or removed until it recorded volumes correctly. It was checked occasionally throughout the work. A second similar metre placed at the end of the absorption train was used to determine the volume of the exit gas.

2 - Temperature Control

Generally the reaction tube was heated electrically, although preliminary work has been done with gas-fired furnaces. Electric furnaces were found more convenient because of the ease of control and absence of fumes and dust. It was found possible to regulate the temperature to within two or three degrees by means of an adjustable slide-wire resistance in series with the furnace winding. A Leeds and Northrup automatic temperature controller was used for part of the work. In the absence of the controller it was found necessary to periodically note the temperature and make the necessary adjustments in resistance in order to maintain the desired temperature.

Two types of furnace were used. In some work it was desired to have the maximum temperature (hot spot) in the centre of the furnace. This was accomplished by winding the furnace tube evenly throughout and building a square or cylindrical heat insulator around this. In a large part of the work the hot spot of the furnace was brought towards the exit end of the furnace. There were two methods of obtaining such a temperature distribution. The heating element could be more closely spaced near the exit end or the heat insulation could be cone shaped. The base of the cone was found to contain the "hot spot".

Fig. I

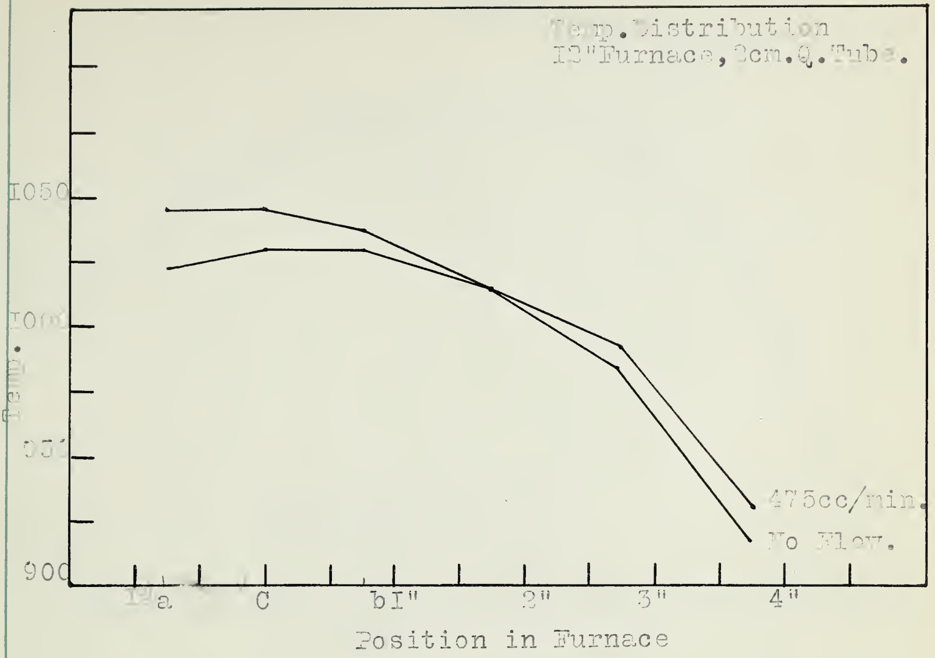

Temp. Distribution
I2"Furnace, 2cm.Q.Tube.
I050
I000
950
900
Temp.
a
C
bI"
2"
3"
4"
475cc/min.
No Flow.
Position in Furnace

Fig. 2

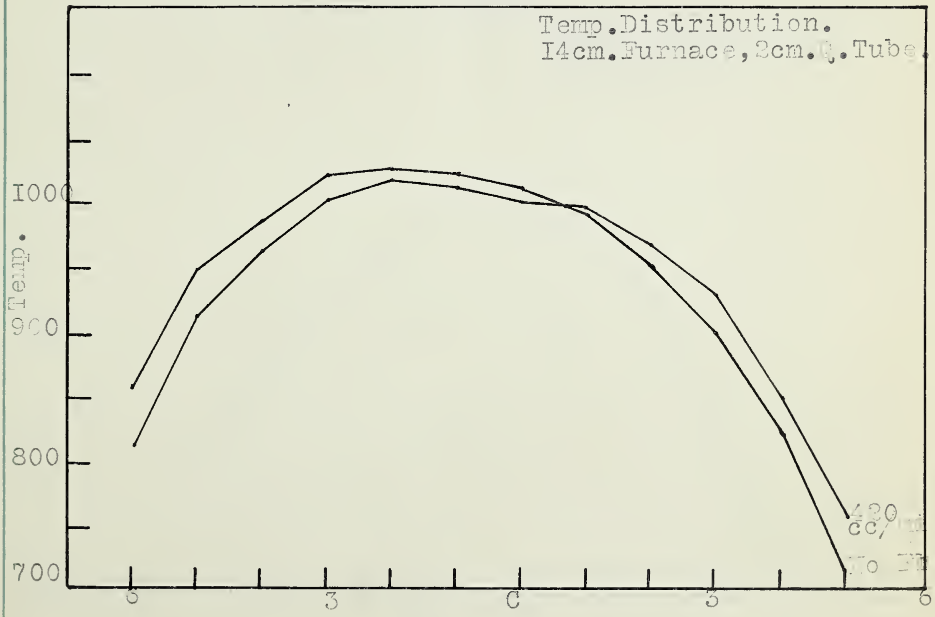

Temp.Distribution.
I4cm.Furnace,2cm.Q.Tube.
I000
900
800
700
Temp.
6
3
C
3
6
420
cc/
No F

Fig.3

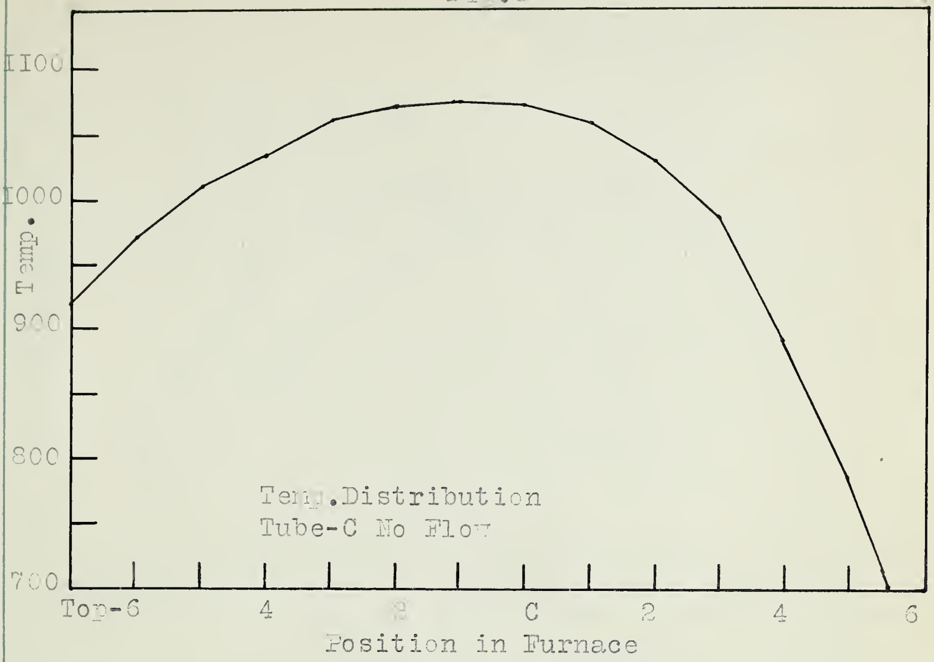

Temp.
1100
1000
900
800
700
Temp.Distribution
Tube-C No Flow
Top-6
4
3
C
2
4
6
Position in Furnace

Fig.4

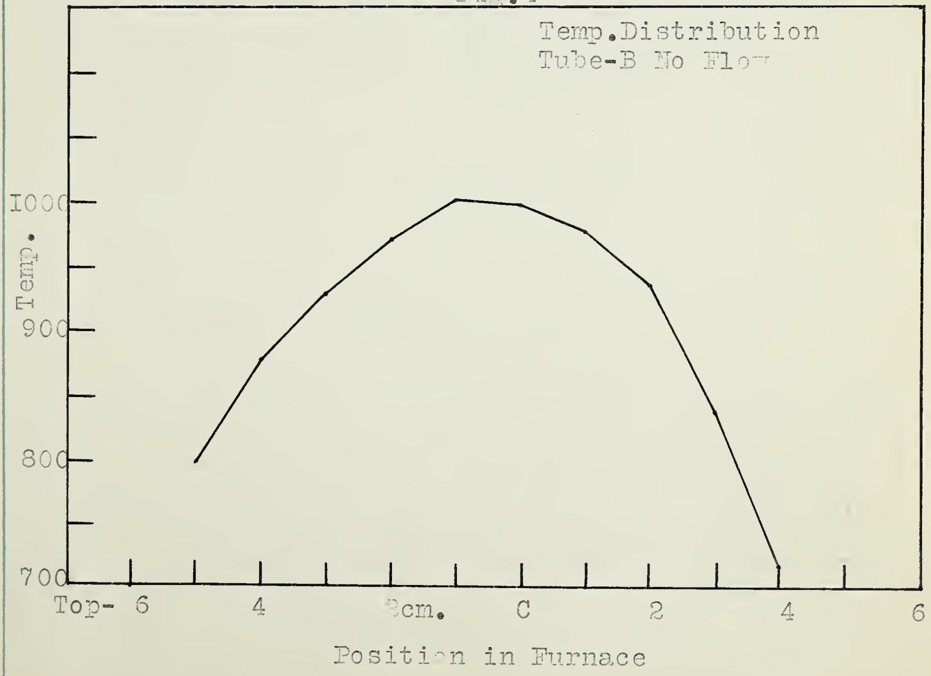

Temp.Distribution
Tube-B No Flow
Temp.
1000
900
800
700
Top- 6
4
3cm.
C
2
4
6
Position in Furnace

Fig. 5

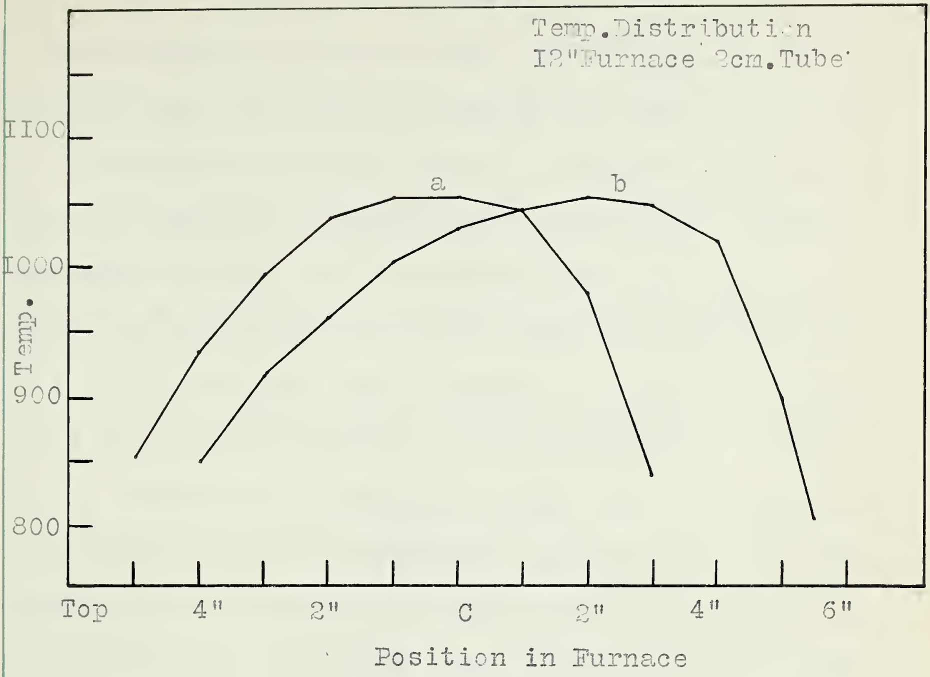

Temp. Distribution
12"Furnace 2cm. Tube
a
b
1100
1000
900
800
Temp.
Top
4"
2"
C
2"
4"
6"
Position in Furnace

Fig. 5 shows the difference in temperature distribution between a furnace with the hot spot in the centre in one case, and removed towards one end in the other.

A gas when passed through a hot tube will not necessarily reach the temperatures of the tube. There is strong evidence to show that conduction of heat from a solid to a gas is controlled by a thin film of stationary gas on the solid surface. The transfer of heat by convection in this film is so slight as to be negligible. There is a large temperature gradient through the film that makes up practically all the difference between the wall temperature and the flowing gas temperature. At rates of gas flow below the turbulent stage there is a second and smaller gradient through the gas, and at rates of flow above the turbulent stage the temperature of the gas is uniform.

Langmuir (19), in studying temperature distribution near a metallic surface, showed the existence of the above-mentioned surface film and measured its thickness. He moved a delicate thermocouple towards a heated silver plate. The couple temperature remained fairly constant until it reached a definite distance from the plate. At this point the temperature rose rapidly to that of the plate itself.

The thickness of the film is inversely proportional to the velocity of the gas past the walls. Heat is

transmitted through this film by conduction. It is largely convection which heats the moving gas. Due to the transparency of gases heat transmission by radiation can be ignored.

Rice (25) gives the following expression for the heat transfer to an ideal gas.

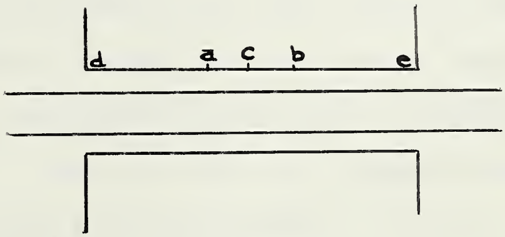
$$W_c = (AR\,{}^{\Delta t}/KD)(\rho DV/u)^{\alpha} \quad \text{watts}$$

where W_c = total convective loss from area A
A = area
R = thermal conductivity of fluid
Δt = difference in temperature
K = experimentally determined
D = dimension of reference to define size of body
V = velocity of flow
u = viscosity of fluid
ρ = density
α = change in density per unit change in temperature.

No more than an approximate calculation can be made with this formula. It is itself an approximation, and moreover, precise data are lacking in the case at hand. The calculation shows, however, even with unfavorable choice of data, that in the experiment reported the maximum temperature difference would be about 100°C.

It was necessary to determine as accurately as possible the temperature which the gas reached in the reaction tube. A thermocouple placed in the path of the gas would not necessarily measure its temperature as a large part of the heat gained by the thermocouple would be due to radiation from the wall of the tube. The thermocouple would not read the wall temperature, however, because of the cooling effect of the gas.

The temperature of the gas was determined in the following manner:



In a horizontal evenly wound furnace, the maximum temperature is in the central part. With a 12" furnace there was found to be a region of uniform maximum temperature 1 1/2" long. The temperature gradient along the tube from this central hot region is at first small, and gradually increases as shown in Fig. 5A.

It was found that with no gas flow the temperature gradient as determined by exploring the entire length of the tube in the furnace with a Pt.-Pt.Rd. thermocouple was not the same on both sides of the middle of the furnace.

The temperature of the end through which the thermocouple entered was found lower than that of the other end. This can be seen in Fig. 2. A careful study of temperature distribution was therefore made.

A furnace similar to that shown in Plate II was used. The furnace tube was heated for a length of 12 cm. A quartz tube 1.5 cm. in diameter was placed coaxial with the furnace tube. Both ends of the furnace were thoroughly lagged. A Chromel-Alumel thermocouple was placed between the quartz and the furnace tube. In this way a check could be kept on the furnace temperature. The necessary adjustments were made in resistance from time to time in order to keep the furnace temperature constant throughout the experiment. A Pt.-Pt.-Rd. thermocouple in a 5 mm. quartz tube was used to explore the furnace.

The four following temperature distribution studies were made:

1. With the furnace vertical the thermocouple was passed through the lower end of the quartz tube.
2. With the furnace vertical the thermocouple was passed through the upper end of the quartz tube.
3. With the furnace horizontal the thermocouple was passed through the left end of the tube.
4. With the furnace horizontal the thermocouple was passed through the right end of the tube.

In each case the opposite end of the tube was plugged to prevent convection currents.

The results are given below:

Position in Furnace	Vertical 1	Vertical 2
Top	891	759
1 cm.	934	825
2	963	911
3	984	958
4	1003	986
5	1011	1002
6	1015	1017
7	992	1019
8	966	1013
9	924	993
10	856	964
11	765	906
Bottom	672	847

	Horizontal 3	Horizontal 4
Left	755	822
1	827	887
2	887	943
3	928	967
4	963	989
5	988	997
6	999	997
7	1008	993
8	997	968
9	980	936
10	946	890
11	893	815
Right	846	746

An examination of the above will show that the shape of the temperature distribution curve will depend on the method of obtaining temperature readings. There are several possible explanations.

1. The thermocouple when projected through the central hot portion of the furnace tends to register high temperatures. Heat may be conducted from the "hot spot" along the thermocouple wires to the junction thus causing an increase in temperature.
2. Considering the diagram P-25, if the junction were placed at D from the side D it showed temperature values lower than the true wall temperature at that point, due to heat loss from the junction along the wires.

Lowering of temperatures due to loss of heat as in (2) would exceed increase in temperature due to gain of heat as in (1), because the temperature gradient between D, and a short distance from D where the temperature is at that of the room, is much greater than between D and C.

In determining the true temperature of the gas, however, it was found that the necessary data were obtained near the centre of the furnace where the heating and cooling effects described above are reduced to a minimum.

If a thermocouple is passed through the furnace entering the quartz tube at E and extending to D (see diagram P-25), it will register a temperature somewhat higher than the true temperature of the walls at that point. When gas is allowed to enter at D it will have a

cooling effect on the couple. Since the gas enters at room temperature the cooling effect will be considerable. This can be determined by noting the temperature with and without gas flow. If now the couple is withdrawn to the middle of the tube, with no gas flow, it will register very nearly the temperature of the walls of the tube at this point. When the gas is allowed to flow it will again have a cooling effect on the thermocouple except in the improbable event of the gas being at the same temperature as the tube wall. The temperature of the tube at E was found to be approximately 700°C. when the centre of the tube was 1000°C. If the gas, in flowing through the tube, has been heated above 700°C. the thermocouple at E will show a temperature greater than 700°C., but not equal to the gas temperature. If the gas were heated to just 700°C. in passing through the 1000°C. region, the thermocouple at E would not change in temperature and 700°C. would be the true gas temperature at this point. There will be a point on the outlet side of the middle in every tube where the temperature of the gas and the wall is the same. The thermocouple will register no rise or fall in temperature at this point when the gas flow is turned off or on. The temperature at this point will be very nearly the true temperature of the gas.

Both horizontal and vertical tubes were studied. The thermocouple was placed coaxial with the tube, care being taken to keep it away from the walls. In Fig. 1 the point C is the centre of the furnace. The thermocouple was inserted from the right or outlet end. The temperature was first taken at the point (a) with no gas flowing. The gas was then turned on at a desired rate (475 cc/min. in thiscase) and after the junction had reached equilibrium the temperature was noted. The gas was turned off and the couple allowed to reach wall temperature when a third reading was made. The last step was necessary as a check on the constancy of temperature of the furnace. Each point on the graph represents a set of readings.

It will be noted that the true gas temperature is some 30°C. below the maximum temperature of the reaction tube. This is true for both the 12" and the 14 cm. furnace.

A full survey of all the furnaces at varyinggas rates was was not undertaken. Sufficient was done, however, to show that the temperature of the gas does not differ by more than 50°C. from the maximum wall temperature at the highest rate of flow used, and the temperature difference decreases greatly with decreasing rates of flow.

3 - Collection of Products of Reaction

Natural gas, when passed through quartz tubes at temperatures above 900°C., yields benzene and tar-like products. These heavier products, on leaving the heated zone of the reaction tube, condense to form tiny globules which leave the tube as a very fine fog. The lighter products, such as benzene, are in the form of a vapor.

The tar fog was found to be very stable and could not be easily removed at rates of gas flow above 100 c.cm. per minute. Settling chambers were impractical because of the very large size required. Condensers at low temperatures from 0°C. to -78°C. did not stop more than a small part of the fog. Glasswool and similar types of filters were of very little use.

The first apparatus devised to collect the oil products consisted of

(1) A 600 cc. Erlenmeyer immersed in hot water to collect the tar.

(2) A second Erlenmeyer in air to collect the naphthalene.

(3) A third Erlenmeyer cooled by snow to take out light oils such as benzene.

This apparatus was found quite ineffective as the oil yield amounted to but 2% by weight of the gas passed.

Therefore an attempt was made to improve the system. The first Erlenmeyer was replaced by a 500 cc. bulb (as shown in Plate II-F.) Two condensers were placed after this. The first was ice-cooled and the second was CO_2 snow cooled. At low rates a part of the tar settled in the trap and benzene condensed in the cooled condensers, but the maximum yield was approximately 5%. At rates much above 100 cc. per minute the yield dropped to 2%.

Attempts were made to precipitate out the oil with the aid of steam. The fog on leaving the reaction tube was intimately mixed with steam from a steam generator. The mixture was passed through a water cooled condenser. It was hoped that the steam, on condensing, would precipitate out the oil. A twelve inch condenser, plugged with glass wool, was found to effectively remove the oil up to rates of 300 cc. per minute. Above this rate it was ineffective. This method of removing the oil, however, could not be used in the work under discussion as it was quite impossible to determine the yields of oil quantitatively.

An attempt was made to drive the fog to the walls of a condenser by means of a tiny centrifuge. A small rotor in a close fitting glass tube was rotated at about 3000 r.p.m. Various shaped rotors were tried but not one was found to successfully deposit the tar fog on the walls

of the container.

The principle of the well-known Cottrell process (8) of electrical precipitation was applied in a simple form. The high tension poles of a 24-watt induction coil were connected to two electrodes in the gas stream and the current in the primary adjusted so that sparking was just prevented.

Initially aluminium plates were used as electrodes. Complete precipitation of the fog was obtained, but as soon as the plates became covered with oil they became ineffective. Smooth metallic substances were not in general satisfactory for this reason and moreover the prevention of violent sparking was difficult. A discharge such as produced incipient sparking was necessary and such a condition is difficult to maintain. Salt solutions in glass tubes, and various other electrodes were used, but were found ineffective for one reason or another.

The precipitator finally adopted was a glass tube 3 cm. in diameter and 18 cm. long. See Plate II-G. A band of copper foil was wound around the middle portion of the tube between the gas entrance and exit tubes. This served as one of the electrodes, the other being coaxial with the tube. Two types of inner electrodes were used. An aluminium rod covered with a thin coat of alundum cement was held in the centre of the tube by

means a rubber stopper. The alundum cement was very fine grained and presented an extremely large number of fine points from which the discharge could escape. The result was a corona discharge with very little sparking. The precipitator as described above worked efficiently for several hours until the alundum covered electrode became saturated with oil. The best and final type of axial electrode, and one of apparently unchanging efficiency, consisted of a 2 mm. aluminium rod covered with alundum cement and inserted in a thin-walled glass tube closed at the inner end. Ultimately the glass is cracked and requires replacement, but this disadvantage is slight compared to the high unchanging efficiency of the electrode.

The recovery of light oil vapors also presented a problem. Condensers of various types, even at -78°C., did not appear to be efficient, and absorption methods were necessary.

Stanley and Nash (26), in their work on the pyrolysis of methane, used silica gel to absorb both the tar and light oil. They determined their yields by measuring the weight increase of the gel and reported yields of 11.5%. The method appeared worthy of investigation. Silica gel was prepared after the method of Holmes and Anderson (16). $Fe\ Cl_3$ was used as precipitant and a hard white gel was

obtained. On using this gel as an absorber the yields (as determined by weight increase of gel) increased to 9%, which was almost double any former yield. An attempt was made to recover the oil from the gel by steaming, but no efficient oil recovery apparatus had been developed up to that time and the percent recovery was low.

Fischer (12) used activated charcoal to recover most of the oil, and took out the last traces of fog with an electrical precipitator placed at the end of the absorption train. He reported yields of 12.9%.

Activated cocoanut charcoal was therefore investigated and the yields, as calculated from weight increase of charcoal, were much higher than those obtained using silica gel. Yields as high as 18% were obtained. Since these were much higher than any reported up to the present time the validity of determining yields by measuring weight increases in the charcoal absorbers was doubted.

Activated charcoal is known to preferentially absorb hydrocarbons (Burrell & Oberfell - 5). If different hydrocarbons are passed as gases or vapors through charcoal the hydrocarbon with the higher boiling point will be absorbed in preference to the low boiling hydrocarbons. Unsaturated hydrocarbons, such as ethylene, have been found to be readily absorbed by charcoal. It is known that in the presence of hydrocarbons no appreciable

amount of hydrogen will be absorbed. The increase in weight of the absorbent charcoal might therefore be greatly different from the weight of oil absorbed.

It was found necessary to make a number of runs in order to study the manner in which oil and gas is absorbed under the prevailing conditions.

The experiment described below was performed towards the end of the investigation under consideration, but it is necessary to include it at this point in order that the results to follow may be rightly interpreted.

Gas was passed through a 1.5 cm. quartz tube which was heated to 1050°C. The rate of flow was kept as constant as possible at about 300 cc. per minute. The absorption train consisted of a trap, an electrical precipitator and a charcoal absorber. These were removed, stoppered and weighed, after approximately 1 cu. ft. of gas had passed. The condensers were then replaced and a second foot of gas passed through them. The gas flow was not stopped during weighings as this changed the condition of the reaction tube which resulted in erratic results. Seven feet of gas were thus passed through. The results are shown in the accompanying table and Fig. 6.

It will be noted that a large part of the unsaturated hydrocarbons is absorbed by the charcoal in the first

cubic foot. After the first foot has been passed the percentage of unsaturated hydrocarbons remains almost constant. By unit yield (and expansion) is meant the yield as calculated by weight increase per cubic foot of gas passed. By total yield is meant the yield as calculated on the total amount of gas passed. The yield on the first cubic foot was 19%. This is excessively high due to gas absorption. This is shown both by the gas analysis and by expansion. The expansion after the first foot amounts to 18.5%. It is possible to calculate the amount of gas absorbed from the data on hand.

An expansion of 18.5% on 0.972 cu. ft.
yields 1.15 cu. feet.

An expansion of 9.0% on 0.972 cu. feet
yields 1.06 cu. feet.

Therefore, amount of gas absorbed

$$= 1.15 - 1.06 = 0.09 \text{ cu. ft.}$$

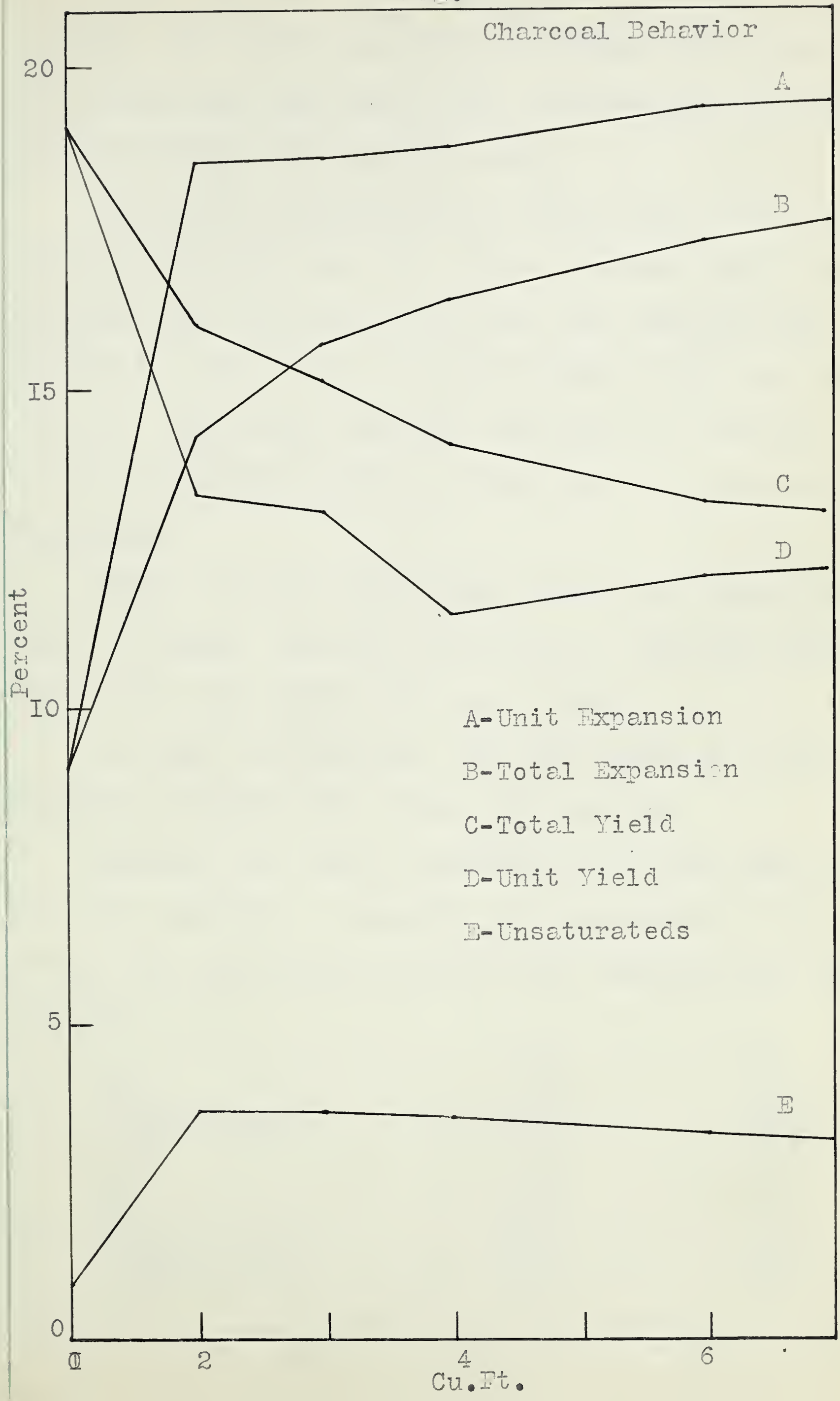
Gas analysis shows the amount of unsaturateds absorbed to be $3.2 - 0.9 = 2.3\% = 0.022$ cu. feet. Therefore more than unsaturateds are absorbed during the first cubic foot.

To learn whether methane and ethane are readily absorbed Viking gas was passed directly from the mains into a condenser containing charcoal. An increase of 2.4 grams per hundred grams of charcoal was noted.

TABLE I

		1	2	3	4	5	6	7
Trap	Unit	.42	.59	0.43	0.37	0.31	0.40	0.36
	Total	.	1.01	1.44	1.81	2.12	2.52	2.88
Electrical Cond.		.54	.53	0.68	0.36	0.46	0.55	0.52
			1.07	1.75	2.11	2.57	3.12	3.64
Charcoal		1.69	.82	0.76	0.91	0.75	0.72	0.73
			2.51	3.27	4.18	4.93	5.65	6.38
Total		2.65	1.94	1.87	1.64	1.52	1.67	1.61
			4.59	6.46	8.10	9.62	11.29	12.90
Vol. Gas		0.972	1.022	1.000	1.000	0.991	0.980	0.929
			1.992	2.994	3.994	4.985	5.965	6.894
Yield		19.1	13.3	13.1	11.5	10.8	12.0	12.2
			16.1	15.1	14.2	13.5	13.3	13.1
Expansion		9.0	18.5	18.6	18.8	18.4	19.5	19.6
			14.3	15.8	16.5	16.85	17.35	17.6
Rate		306	290	295	290	312	290	272
Time in Hours		1.5	1.67	1.60	1.57	1.50	1.63	1.616
Unsaturated		0.9	3.6	3.6	3.5	3.5	3.2	3.1

Fig.6


Charcoal Behavior
A
B
C
D
E
A-Unit Expansion
B-Total Expansion
C-Total Yield
D-Unit Yield
E-Unsaturateds
Percent
20
15
10
5
0
0
2
4
6
Cu.Ft.

This would indicate that undecomposed methane is absorbed. The small quantities of ethane and propane in the Viking gas have been found to decompose on being passed through the reaction tube.

In several experiments in which from 5 to 7 cubic feet of gas were used the oil was steamed out of the charcoal and the gas driven from the charcoal was measured. This volume varied between 0.055 and 0.066 cu. ft. This would indicate that part of the gas which is absorbed in the initial part of a run is later displaced.

After 7 cu. ft. have been passed the total yield is still 1% higher than the unit yield. The unit yield represents very nearly the true yield.

In order to determine the gas remaining in the charcoal, samples were taken and analysed.

Analysis (a) below represents the first gas driven from the charcoal. Analysis (b) represents the gas driven off just as the first oil is removed from the charcoal.

	(a)	(b)
CO_2	7.8	10.1
Unsaturateds	36.0	48.6
O_2	-	0.7
H_2	5.4	-
CO	2.2	2.9
CH_4	24.6	6.9
Higher H.C.	24.0	30.8
N_2	0.0	0.0

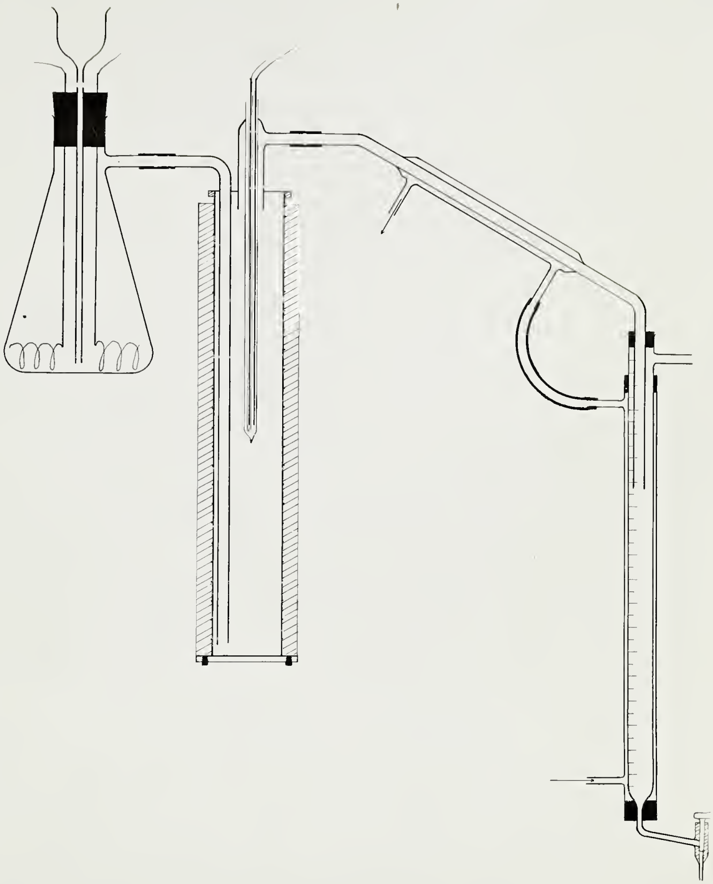
The above analyses show that the gases absorbed in the greatest quantity are the unsaturateds. Methane and Hydrogen are also absorbed to an appreciable extent but they are found to be much more readily displaced from the charcoal than the unsaturateds.

A dense vapor with a pungent odor which did not condense on leaving the charcoal was noted but not identified. It is believed that this vapor accounts for the high percentage of hydrocarbons higher than methane in the combustion analysis.

The apparatus used for oil recovery by steam distillation is shown on page 42, Plate I. Steam was generated in a 600 cc. Erlenmeyer flask by means of an electric heating element. The charcoal was kept in a brass cylinder 2 inches in diameter and 14 inches long. A heating element was wound around this. Both heat and electrical insulation were effected by means of asbestos. A cap was screwed onto the upper end of this cylinder. It had brazed into it a steam delivery tube which extended to the bottom of the cylinder. A second larger tube accommodated a thermocouple well and also acted as exit tube for the vapors. This was attached to a small water cooled condenser which in turn was attached to a water jacketed burette.

The charcoal was poured into the lower end of the cylinder, which was then capped by a brass plate firmly

PLATE I.



attached by 6 screws. Steam was generated and at the same time the cylinder was gradually heated up to 350°C.

It was found possible to remove the light oil without using superheated steam, but it took a long time. In many cases oil of a much higher boiling point than that of benzene was included in the charcoal and it was found difficult to remove this, even at 350°C.

Usually 90% of the weight increase in the charcoal was recovered as light oil. The light oil makes up approximately 50% of the total oil. It has been found that 95% of the yield as determined by weight increase is recoverable.

Plate II shows the apparatus as used for most of the work. Viking gas, when used, was taken directly from the mains. Turner Valley gas was taken either directly from a high pressure storage cylinder or first passed into a 10 cu. ft. gas holder. The gas flow could be more conveniently adjusted when the source of supply was the gas holder.

The gas flow was regulated by observation of the flow metre A. It then passed through the gas metre and into the reaction tube C. Part of the tar produced settled in the trap F. The remaining tar "fog" was removed by the electrical precipitator. The precipitator was found to have no effect on the oil or residual gas.

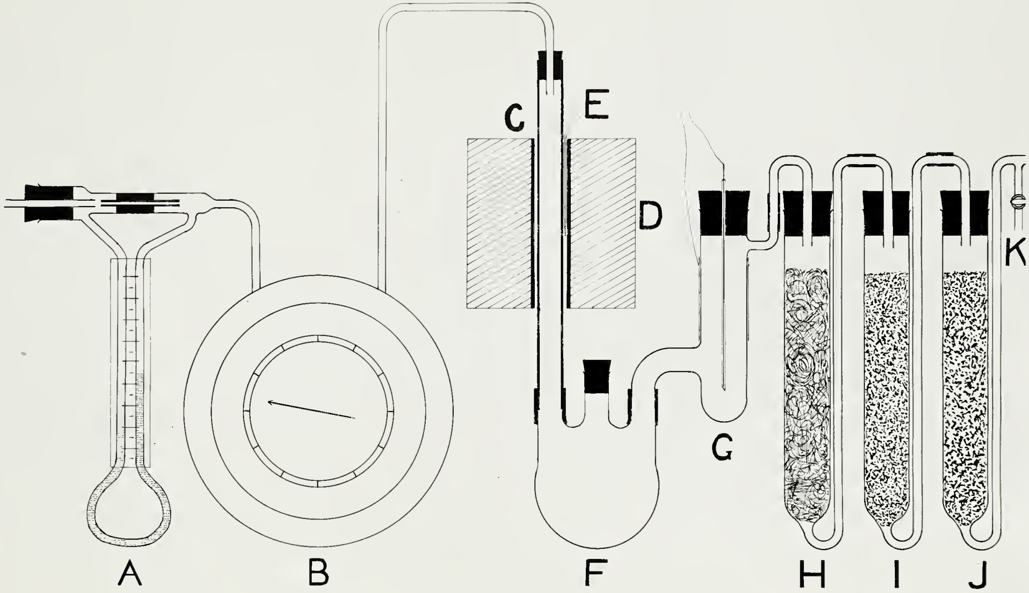


PLATE II

This was shown by taking gas samples, first with the precipitator running, then with the precipitator cut out. In each case the residual gas sample which was taken at K was found to be the same on analysis. It was found most convenient to place the precipitator before the charcoal as it was difficult to remove part of the tar collected by the charcoal.

An air cooled condenser filled with glass wool served to collect part of the naphthalene as white flaky crystals. Two charcoal condensers followed. The first contained fresh charcoal, while the second contained used, but not oil-saturated, charcoal. Usually a 5% weight increase due to adsorption of gas and oil in a previous experiment had taken place. The charcoal was found efficient in absorbing vapors amounting to 25% of its weight so that a liberal margin was provided. In some work this second condenser was air-cooled and in some ice-cooled. It appeared to work as efficiently air-cooled as ice-cooled. Its purpose was to determine the efficiency of the first charcoal absorber. Since this second charcoal absorber was saturated with gas and contained some oil, it registered no weight increase when the first charcoal absorber was working efficiently.

Gas samples were taken at K by the downward displacement of a 50% glycerine in water solution.

A second meter was placed beyond K and was used to

determine gas expansions. This second meter is not shown in Plate II.

When a run was to be made the trap, precipitator, and condensers were weighed. They were then set up as shown in Plate II. The furnace was brought to the desired temperature and the rate of flow adjusted to the appropriate value.

The desired volume of gas, 100 to 700 litres, was then passed through the apparatus. Towards the end of the run gas samples were taken. At the end of an experiment both meters were read and the condensing system weighed again.

4 - Analysis of Products

In calculating the percent yield, the oil was assumed to be benzene and to be produced by means of the overall reaction

$$6\ CH_4 \longrightarrow C_6H_6 + 9H_2$$

$$(6 \times 22.4) \text{ litres } CH_4 \longrightarrow 78 \text{ grams } C_6H_6$$

$$1 \text{ litre} \longrightarrow 0.58 \text{ grams}$$

The temperature and pressure were taken to be 22°C. and 705 mm. respectively. One litre under existing laboratory conditions would therefore yield 0.503 grams benzene if the yield were 100%. As the volume of gas used in an experiment was known, and also the weight of the oil, the yield could be calculated.

One possibility of error in this determination was due to the fact that half the oil was tar. However, a large part of the tar was naphthalene and the remainder anthracene and like bodies.

For naphthalene as above

$$10\ CH_4 \longrightarrow C_{10}H_8 + 16\ H_2$$

$$1\ \text{litre}\ CH_4 \longrightarrow 0.57\ \text{grams}\ C_{10}H_8$$

Very similar figures are obtained for the other polyneuclear unsaturated hydrocarbons. Therefore no appreciable error results from the calculation of yield by the above method. The error such as it is would give a calculated yield less than the true yield.

Yields are also stated in gallons per 1000 cu. ft. In this case the actual oil obtained per cu. ft. is converted to gallons per 1000 cu. ft. The uncorrected gas volume as read from the gas meter is used in this determination. The density of the oil is assumed to be 0.9 with reference to water.

The gas samples were analysed on a Bureau of Mines type of gas analysis apparatus. The unsaturated hydrocarbons were removed with fuming sulfuric acid, the hydrogen with copper oxide and the methane and ethane were determined by combustion with oxygen. At least one analysis was made of each run.

An acetylene determination was made using a modification of the method of Ross and Trumbull (23). A measured volume of gas (usually 270 cc.) was bubbled slowly through a 5% neutral solution of silver nitrate when the following reaction occurred:

$$C_2H_2 + 3AgNO_3 \longrightarrow C_2Ag_2 \cdot AgNO_3 + 2HNO_3$$

The silver acetylide formed a white precipitate. The excess silver nitrate was precipitated by adding a slight excess of 5% sodium chloride solution. The nitric acid formed, as shown in the above equation, was determined by adding an excess of 0.1 N Na OH and titrating back to the end point with 0.1 N HCl. Methyl Orange was used as indicator.

Other than distillation analysis, no tests have been carried out on the light oil or tar products. The light oil was obviously benzene, toluene and naphthalene with only traces of other compounds. Distillation in a good fractionation column showed clearly the presence of these compounds; the first being greatly in excess. Distillation of the tar showed naphthalene anthracene probably phenanthene and a hard pitch residue which boiled quietly yielding a red oil.

IV - RESULTS

The reaction tubes will be described in turn. The method of presenting data can be observed from a study of Table II, P. 52. The rate of gas flow is given in cubic centimetres per minute and the volume of gas used for each experiment is given in litres. It was impossible to determine the time of the reaction of the gas, due to several difficulties as discussed above. Instead of stating the time of reaction; the length of time the gas remains within the furnace region of the reaction tube is given. Gaseous products are stated in percentage of residual gas. The weight of oil obtained per run, and the calculated percentage yields, are stated.

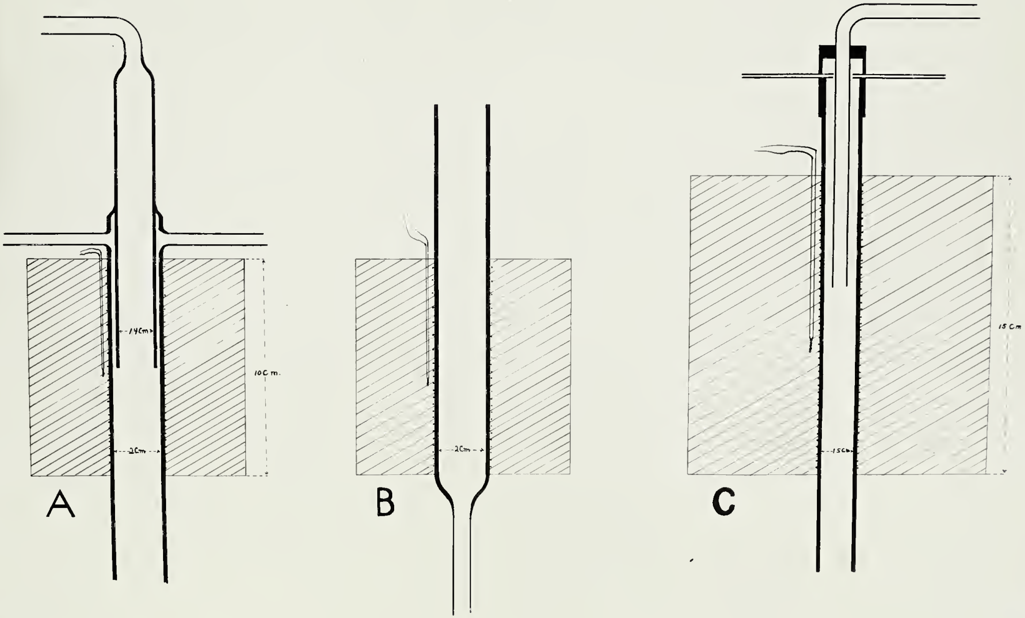


PLATE III

A - Viking Gas

1. Preliminary Work

It was stated above, that during the earlier work no efficient system to absorb the products of pyrolysis had been developed. This resulted in discouragingly low yields now known to be false. The work was of value, however, in determining the relations of temperature and rate of flow on the nature of the gas produced.

The tube used is shown in Plate III, B. 50. It is a quartz tube with an internal diameter of two centimeters. A 0.5 cm. tube is sealed onto the exit end. The gas entered by a ·7 cm. tube which passed through a close fitting rubber stopper in the upper end of the tube (not shown in the diagram). The inlet tube extended to the level of the upper end of the furnace winding. The gas in this manner did not come into intimate contact with the walls until it reached the hotter part of the reaction tube. Nichrome wire was used as the heating element, and this was wound directly onto the reaction tube as illustrated in the diagram. There were four turns of wire per cm. at the exit end, and two per cm. at the top of the furnace. The tube was wound for a length of 10 cm. The termperature distribution curve is shown in Fig. 4.

TABLE II

TUBE B - 1000°C.

Run	Rate of Flow	Time in Furnace	Vol. Gas	Expan-sion	Acety-lene	Unsatu-rated	Hydro-gen	Methane	Total Oil	Yield
#	cc/mm	sec.	Litres	%	%	%	%	%	Gms.	%
47	48.0	39.0	13.7	15.5	0.37	2.9	23.2	71.2	0.36	5.2
48	74.0	25.2	82.3	11.0	0.43	2.8	17.0	73.5	2.41	5.8
49	104	18.0	135.0	11.9	0.41	3.2	15.5	74.5	3.78	5.6
50	141	13.3	55.5	7.6	0.52	3.4	16.1	74.7	0.82	2.9
TUBE B - 950°C.										
40	21	89.2	19.8	-	-	2.2	29.7	58.5	0.34	3.4
44	23.5	79.8	18.08	-	0.29	2.5		74.7	0.35	3.8
24	100	18.8	134.2	7.2	0.46	-		-	3.78	5.6
38	100	18.8	-	-	-	3.0	14.8	77.0	2.89	-
25	110	17.1	141.3	7.7	0.46	3.3	15.5	74.5	-	-
36	122	15.3	185	5.7	0.36	3.9	12.6	79.5	2.20	2.4
31	180	10.4	240.5	3.3	0.32	3.3	7.8	84.8	2.21	1.8

Fig. I

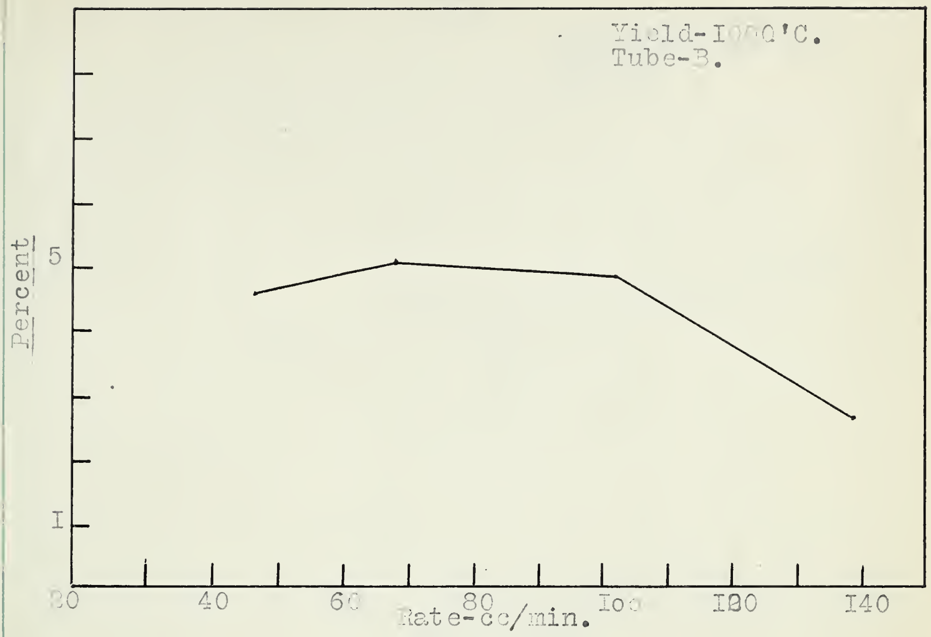

Yield-I000'C.
Tube-B.
Percent
5
I
20
40
60
80
Ioo
I20
I40
Rate-cc/min.

Fig. 2

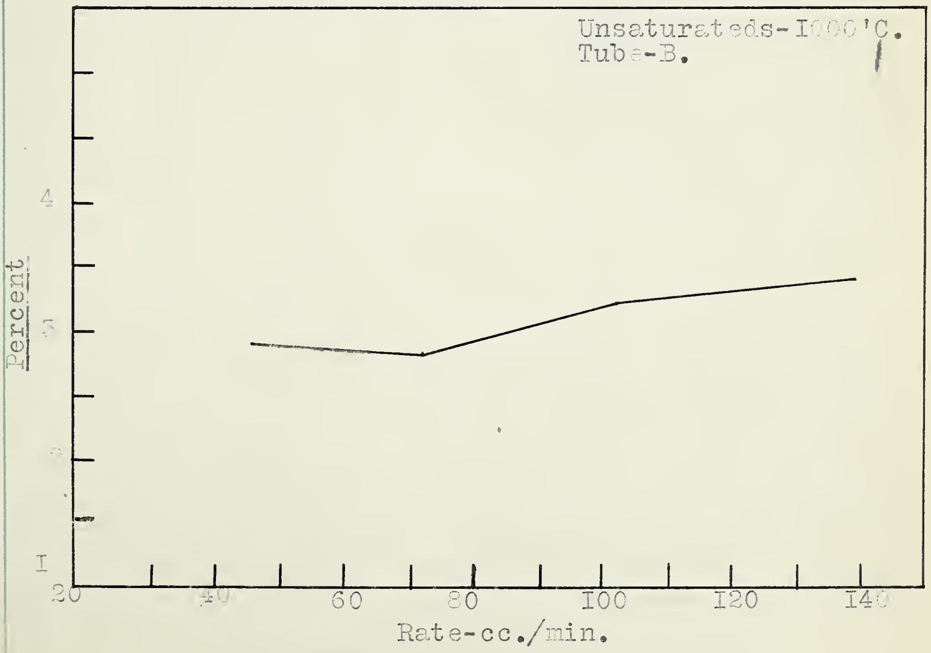

Unsaturateds-I000'C.
Tube-B.
Percent
4
3
2
I
20
40
60
80
I00
I20
I40
Rate-cc./min.

Fig.3

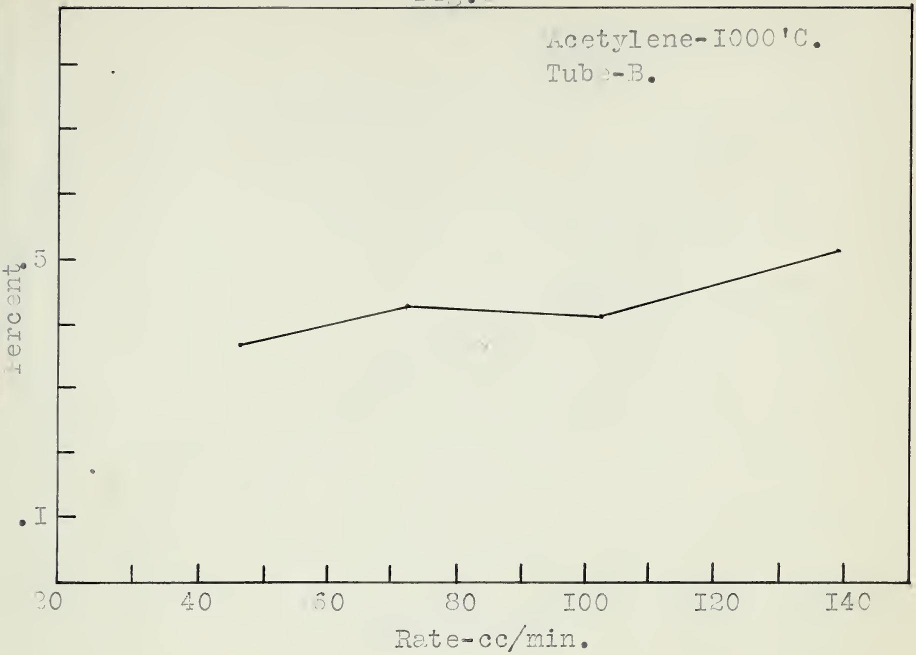

Acetylene-I000'C.
Tube-B.
Percent
.5
.I
20
40
60
80
I00
I20
I40
Rate-cc/min.

Fig.4

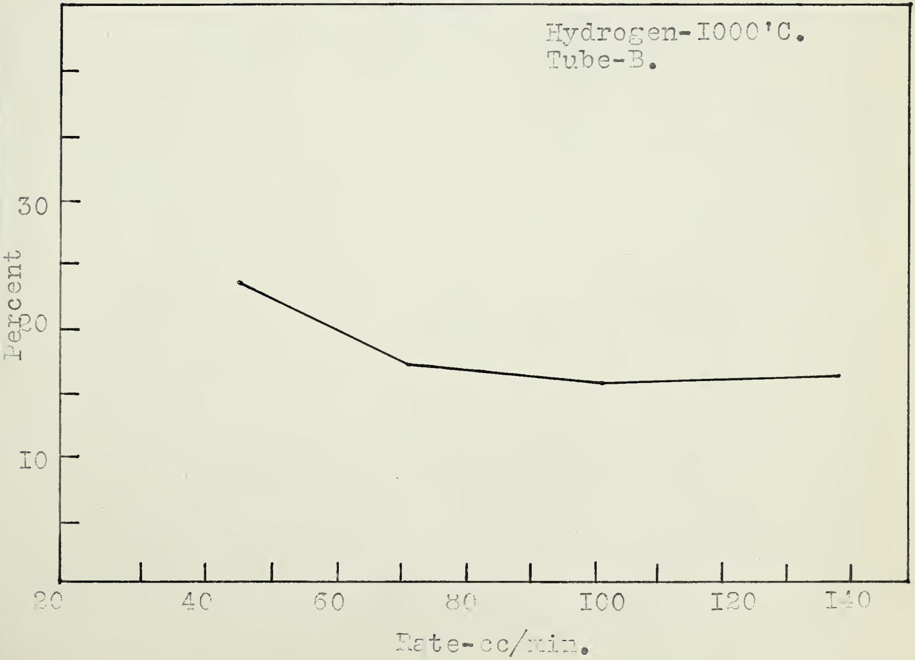
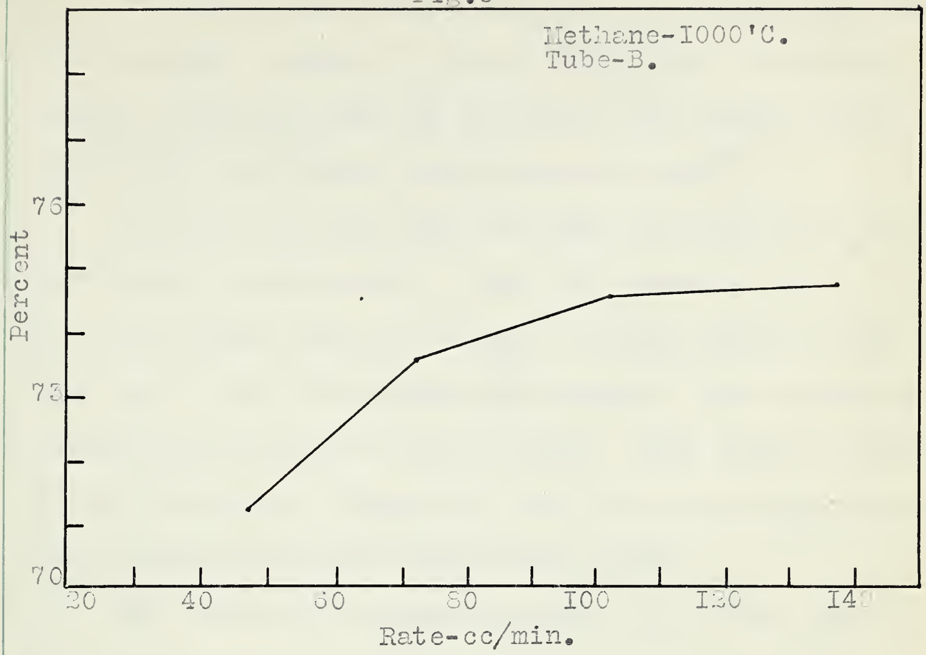

Hydrogen-I000'C.
Tube-B.
Percent
30
20
I0
20
40
60
80
I00
I20
I40
Rate-cc/min.

Fig.5


Methane-I000'C.
Tube-B.
Percent
76
73
70
20
40
60
80
I00
I20
I40
Rate-cc/min.

The absorption train consisted of the 500 cc. trap and an empty condenser cooled by CO_2 snow in alcohol. Rates of flow of from 48 to 141 cc. per minute were used with the furnace temperature at 1000°C.

It will be noted that at rates of flow up to 100 cc. per minute,considerable of the oil deposited out. At 141 cc. per minute there is a drop in yield which is not real, but due to the decreasing efficiency of the collecting system at the higher rate of flow. Much higher normal yields have been obtained at this rate and temperature with a more efficient condensing system.

The results are shown in Table II, P. 52, and Figs. 1-5.

2. Tube A Using Silica Gel

In their work on the pyrolysis of methane, Stanley and Nash (26) used silica gel to absorb the oil production. They found it efficient for the rates of flow which they employed.

Two sets of runs, one at 950°C. and the other at 1000°C. are given below. The apparatus used was a trap and a silica gel condenser. At the time of this work no efficient electrical precipitator had been devised.

The results shown below are not necessarily an indication of the maximum efficiency of silica gel.

TABLE III

TUBE A - 950°C. - USING SILICA GEL.

Run	Rate of Flow	Time in Furnace	Vol. Gas	Expansion	Acetylene	Unsaturated	H_2	CH_4	Total	Yield
#	cc/mm	sec.	Litres	%	%	%	%	%	Gms.	%
69	127	14	45.5	9.3	-	2.5	17.4		1.53	6.7
68	150	12	53.3	8.8	0.48	3.0	16.1		2.16	8.0
70	151	12	53.6	8.4	0.39	2.8	17.0		0.84	3.1
71	175	10	73.0	8.3	0.43	3.1	13.2		2.53	6.9
67	210	3.5	95.0	8.0	-	3.2	12.3		3.30	6.9
72	241	7.5	48.0	6.5	0.30	-	11.7		1.58	6.5
			TUBE A - 1000°C. - USING SILICA GEL.							
73	220	8.0	75.2	11.6	0.58	3.6	21.3		3.01	8.0
75	282	6.4	93.0	10.5	0.57	3.8	20.4		3.32	7.1
77	307	5.8	115.0	9.0	0.65	3.9	16.0		2.98	5.2
83	340	5.3	40.7	-	-	-	-		1.29	6.3
79	360	5.0	114.0	-	0.65	3.3	14.3		2.79	4.9

Fig.6

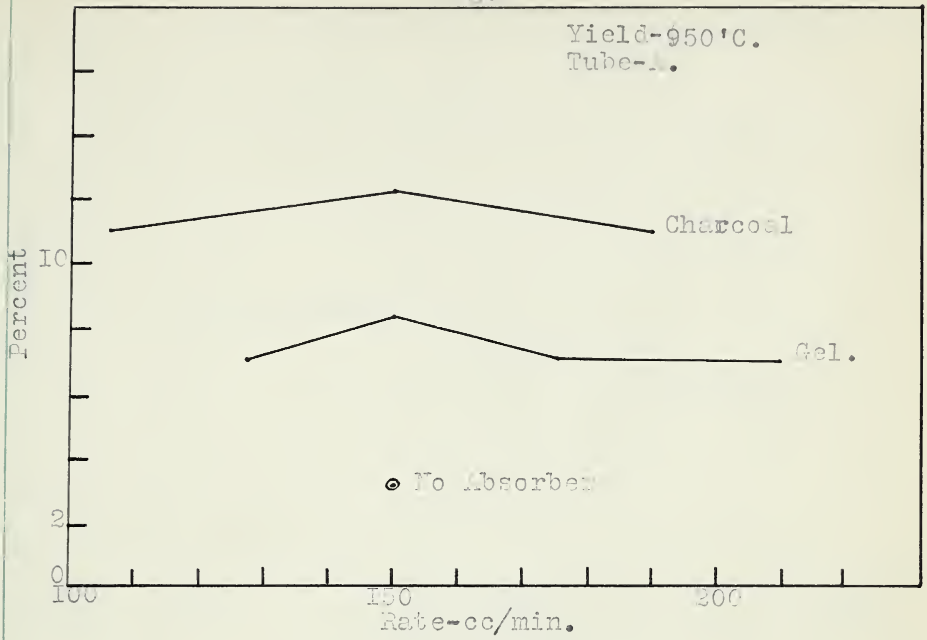

Yield-950'C.
Tube-A.
Charcoal
Gel.
No Absorber
Percent
10
2
0
100
150
200
Rate-cc/min.

Fig.7

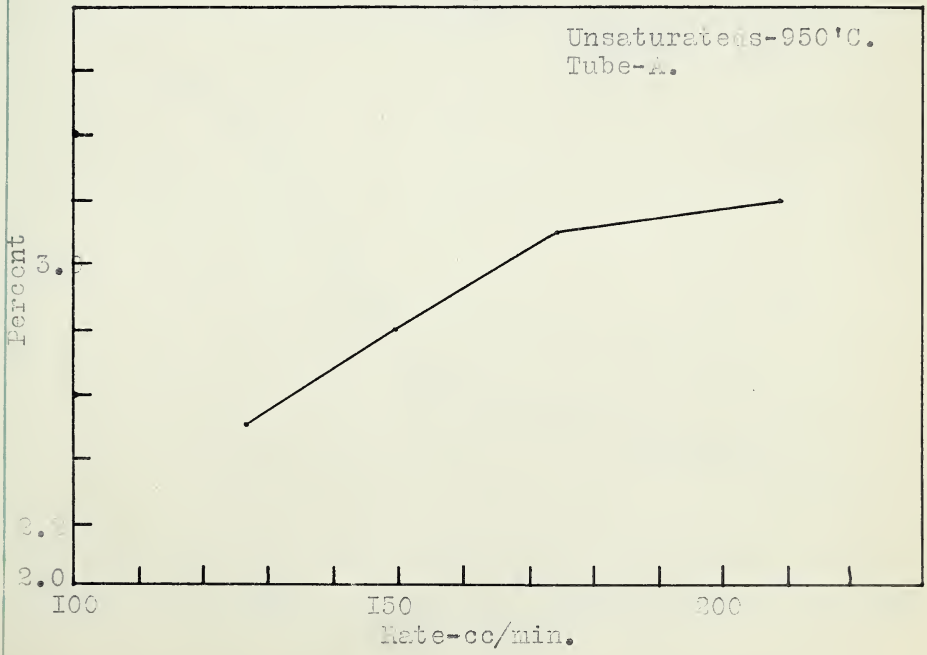

Unsaturateds-950'C.
Tube-A.
Percent
3.0
2.2
2.0
100
150
200
Rate-cc/min.

Fig.8

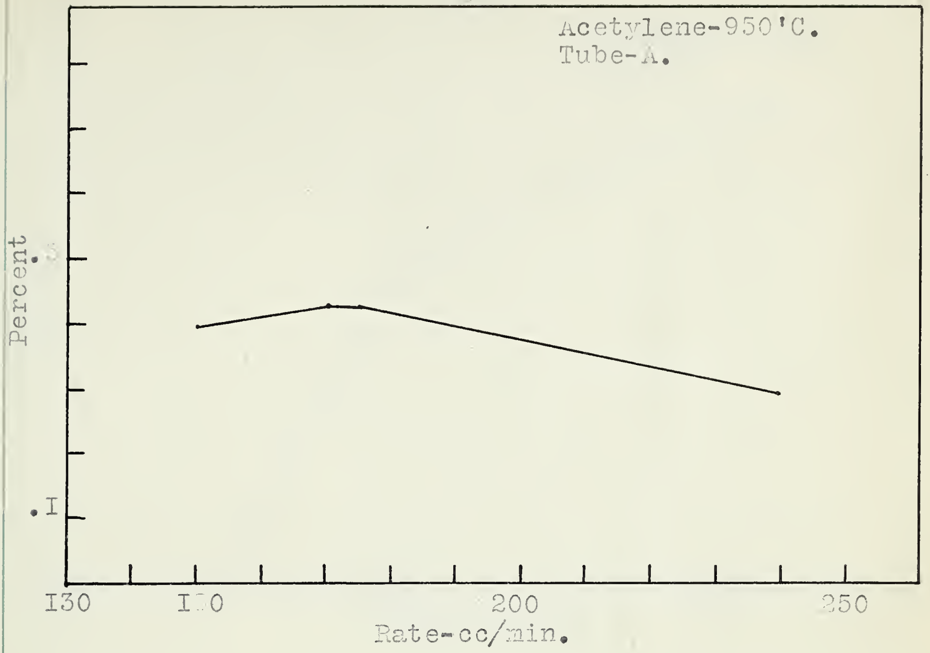

Acetylene-950'C.
Tube-A.
Percent
.5
.I
I30
I50
200
250
Rate-cc/min.

Fig.9

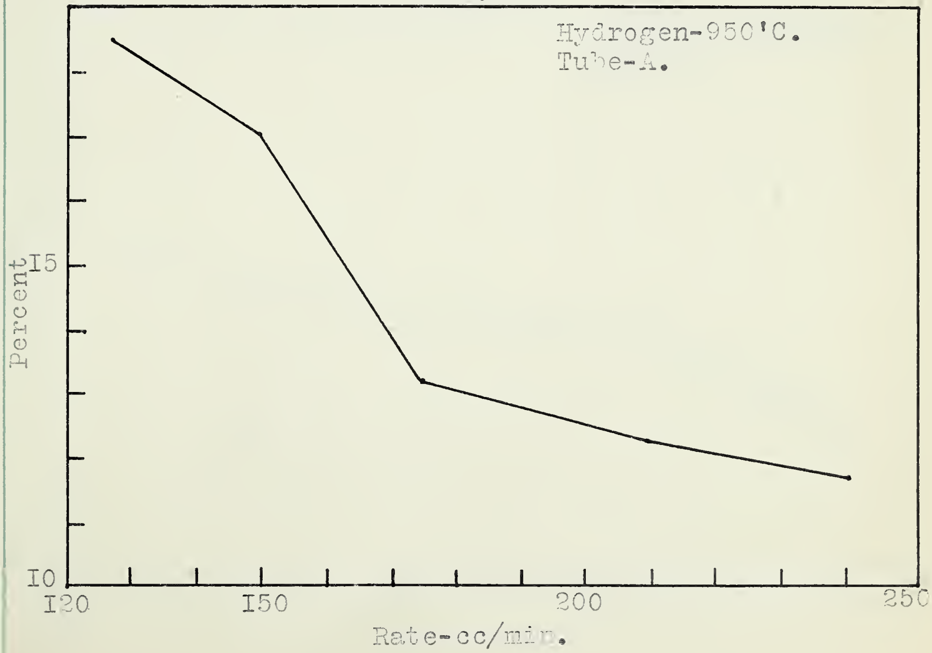

Hydrogen-950'C.
Tube-A.
Percent
I5
I0
I20
I50
200
250
Rate-cc/min.

Fig. 10

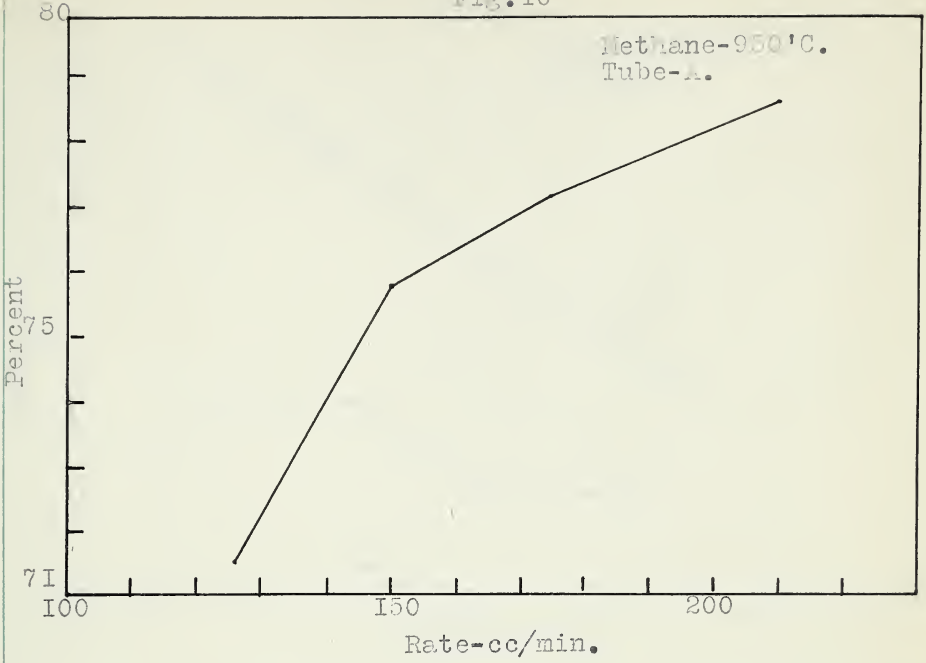

Methane-950'C.
Tube-A.
80
75
71
Percent
100
150
200
Rate-cc/min.

Fig. 11

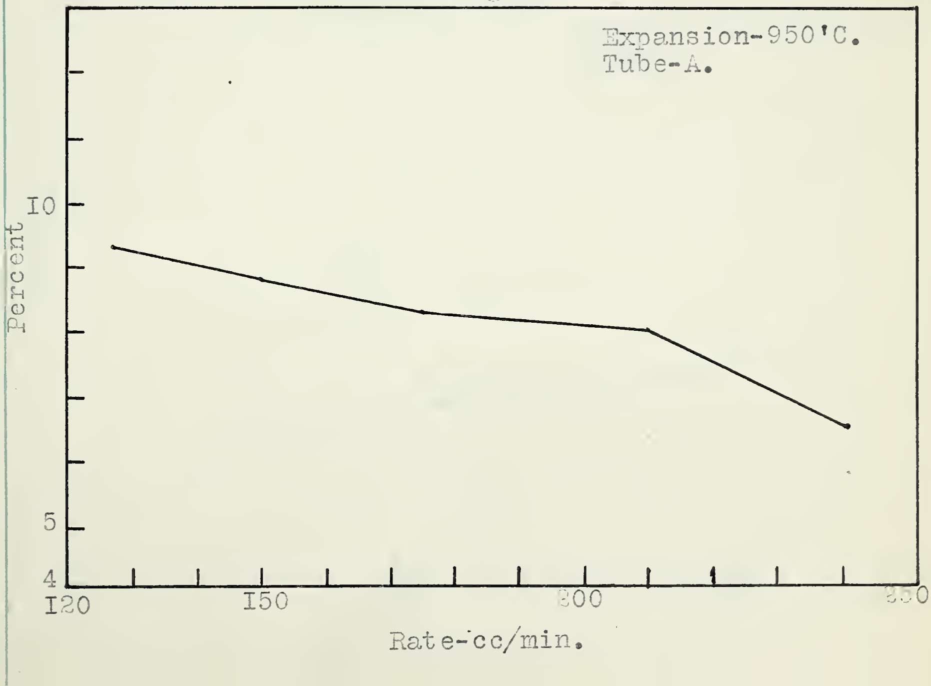

Expansion-950'C.
Tube-A.
10
5
4
Percent
120
150
200
250
Rate-cc/min.

Fig.12

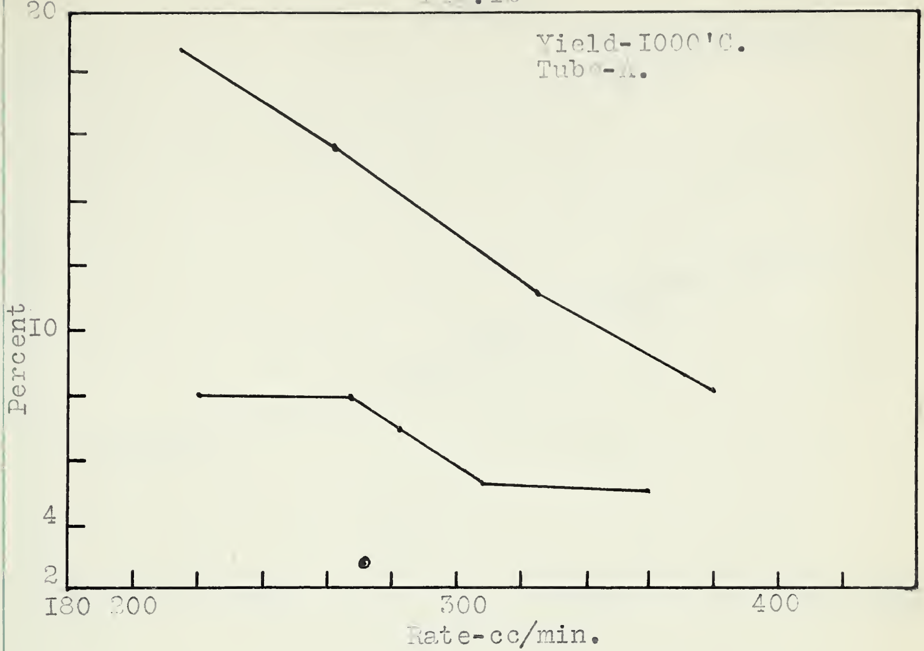

Yield-1000'C.
Tube-A.
Percent
20
10
4
2
180
200
300
400
Rate-cc/min.

Fig.13

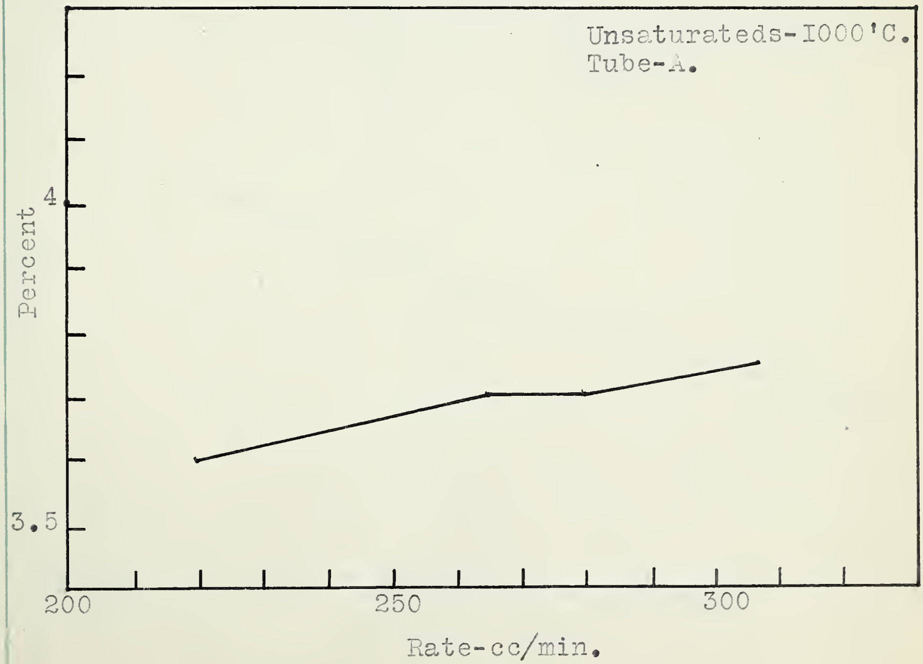

Unsaturateds-1000'C.
Tube-A.
Percent
4
3.5
200
250
300
Rate-cc/min.

Fig. I4.

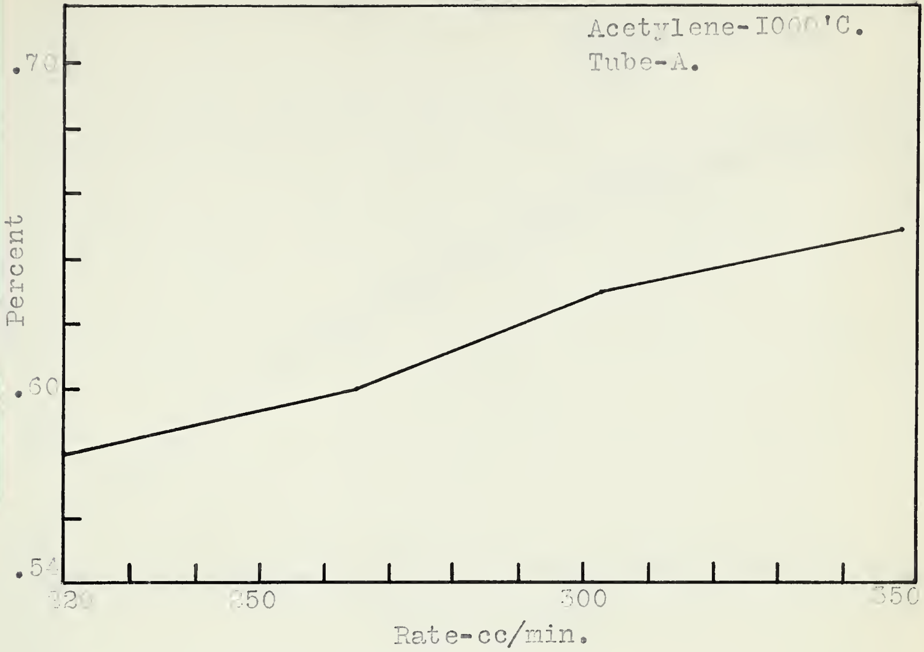

Acetylene-I000'C.
Tube-A.
Percent
.70
.60
.54
220
250
300
350
Rate-cc/min.

Fig. I5

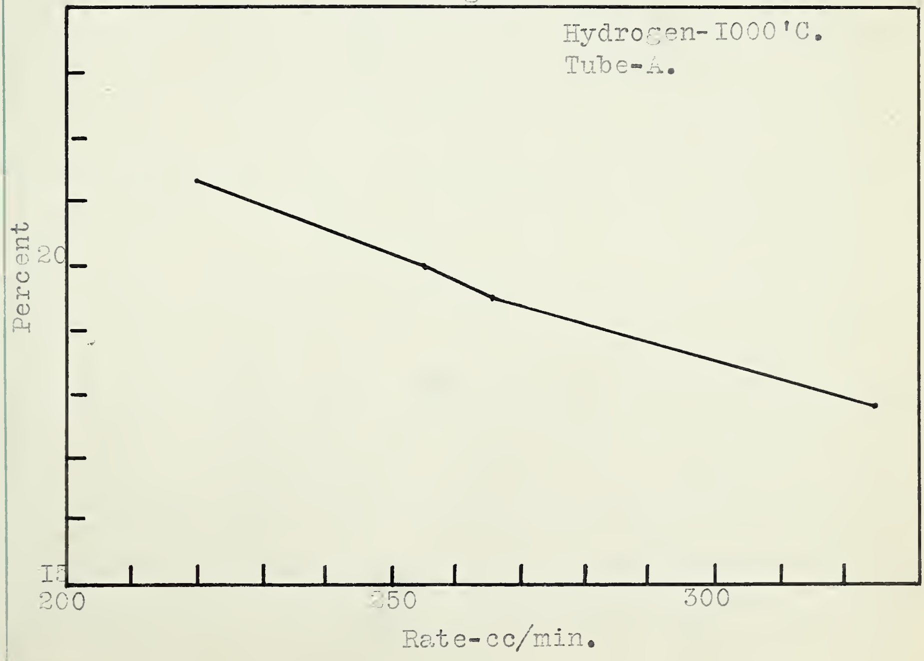
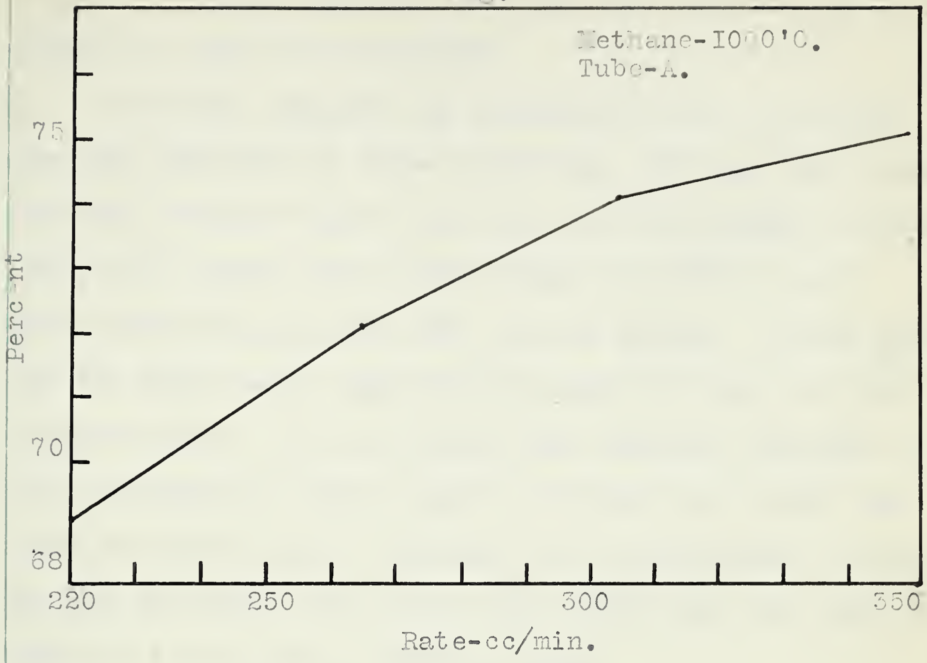

Hydrogen-I000'C.
Tube-A.
Percent
20
I5
200
250
300
Rate-cc/min.

Fig. I6


Methane-I000'C.
Tube-A.
75
70
68
Percent
220
250
300
350
Rate-cc/min.

However, the gel used in this work was found to be inferior to activated charcoal.

Ray (24) compared the absorption power of silica gel and charcoal at rates of 500 and 1000 cc. per minute. He used benzene vapors and found that 100 grams of charcoal will absorb 43.4 grams benzene at 500 cc. per minute and 32 grams at 1000 cc. per minute. Silica gel, on the other hand, was found to absorb 12 and 9.4 grams respectively. He also stated that charcoal absorbed oil in preference to water vapor, but that the reverse was true for silica gel. Contrary to the statements of Ray, Holmes and Elder (17) claim that silica gel will absorb 156% of its weight of benzene vapor.

Table III, P. 57, and figures 6-16 show the results obtained from silica gel. In this work Tube A (Plate III) was used. It was a quartz tube 2 cm. internal diameter. Into this was sealed a second smaller tube as illustrated. It was a 14 mm. tube and left a 10 mm. space between the two tubes. This smaller tube extended into the larger tube, and terminated in the centre of the 10 cm. furnace which was wound similarly to tube B. Two side arms were sealed into the upper end of the large tube. This tube was designed for the study of various gas mixtures, but unfortunately it was destroyed before this work was accomplished. In the work under discussion it was used with the side arms sealed off.

Several points of interest are brought up in Table III and the accompanying graphs. In Fig. 6, yields with charcoal and glass wool as condensers are inserted to compare with the gel curve. Fig. 12 is a similar curve for the yields at 1000°C. The charcoal curve is included to demonstrate high false yields due to gas absorption by the charcoal. In the table, runs #68 and 70 are placed side by side in order to compare ice-cooled silica gel with CO_2 cooled glass wool as condensers. It can be noticed that at a rate of 150 cc. per minute glass wool is quite inefficient.

Gas adsorption by gel can be shown to take place by comparing runs #83 and #77. In #83, 40.7 litres of gas were passed at a rate of 340 cc. per minute and a 6.2% yield was obtained. In #77, at a lower rate, but with 115 litres of gas to the run, the yield dropped to 5.3%.

3. Tube A

A set of runs was made at 1050°C. using charcoal to absorb the oil vapors. The reaction tube used has been described above. The rates used varied from 340 to 600 cc. per minute and the volume of gas used was in each case more than 100 litres. Two quite long runs are included, #105 and 106. It is believed that 11.9 and 10.1% respectively represent a very close approximation to the

TABLE IV

TUBE A - 1050° C.

Run	Rate of Flow	Time in Furnace	Vol. of Gas	Expansion	Acetylene	Unsaturated	H_2	Total	Yield
#	cc/mm	sec.	Litres	%	%	%	%	Grms.	%
105	340	5.3	400	12.8		3.1	29.6	23.97	11.9
106	420	4.3	520	-	0.65	3.0	-	26.30	10.1
90	430	4.2	111.6	-	0.84	-	22.2	7.08	12.6
89	440	4.1	104.0	11.1		-	21.4	6.59	12.6
114	500	3.6	138.0	8.2		3.5	-	9.26	13.3
115	600	3.0	106.7	8.5		3.6	22.5	6.69	12.5

Fig.I7

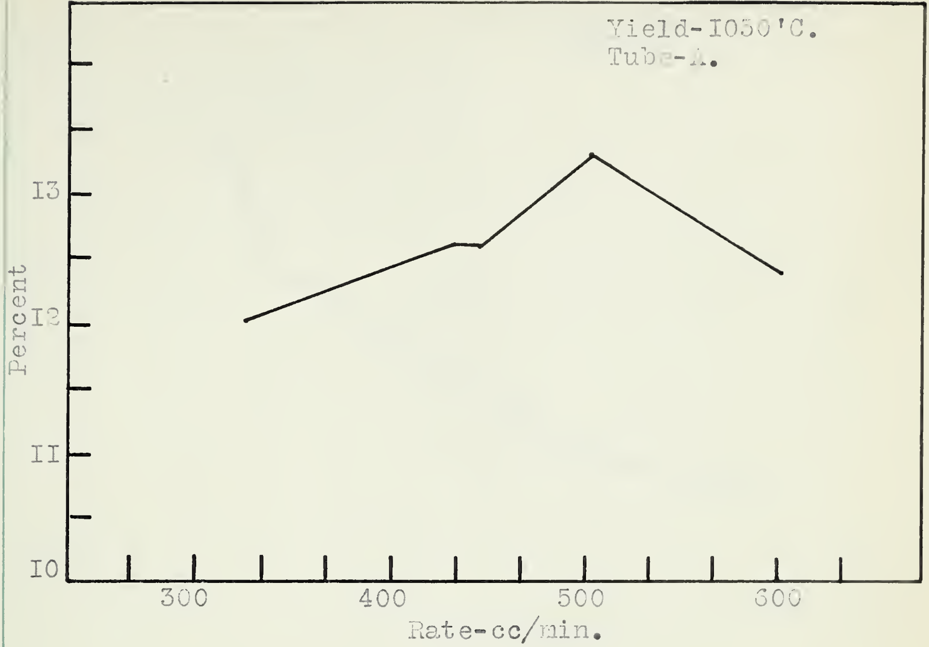

Yield-I050'C.
Tube-A.
Percent
I3
I2
II
I0
300
400
500
600
Rate-cc/min.

Fig.I8

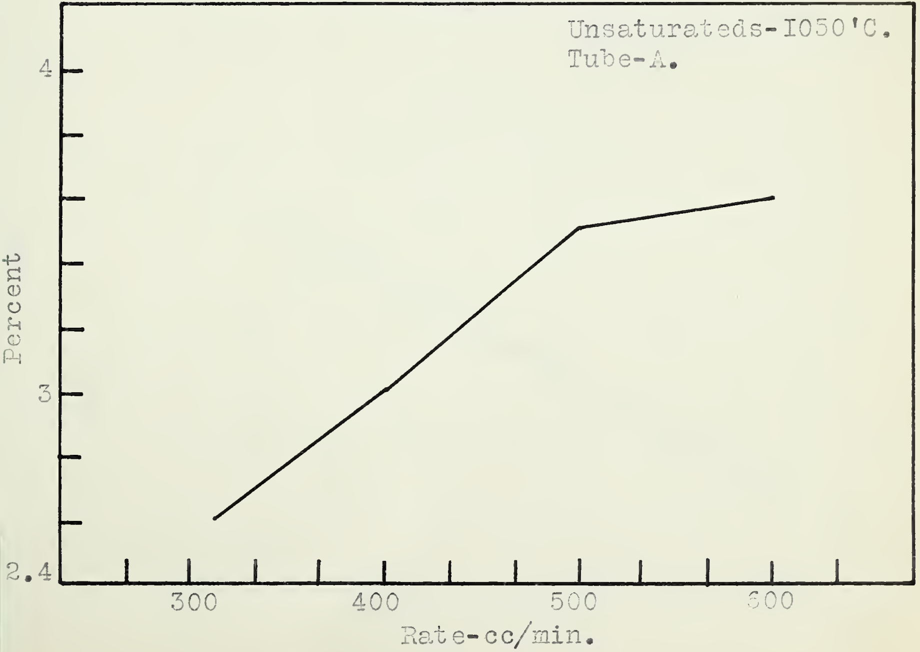

Unsaturateds-I050'C.
Tube-A.
Percent
4
3
2.4
300
400
500
600
Rate-cc/min.

Fig.I9

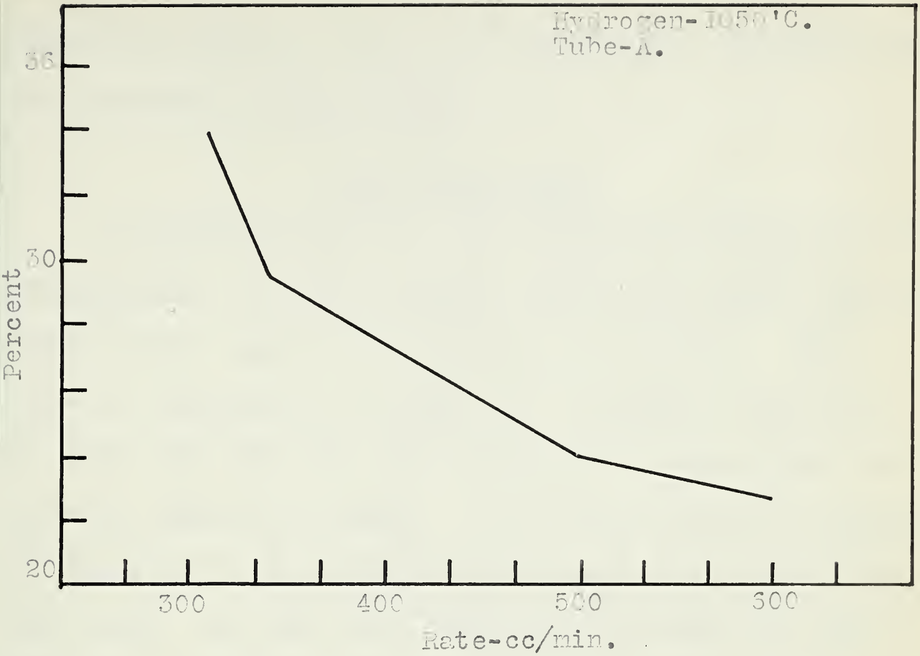
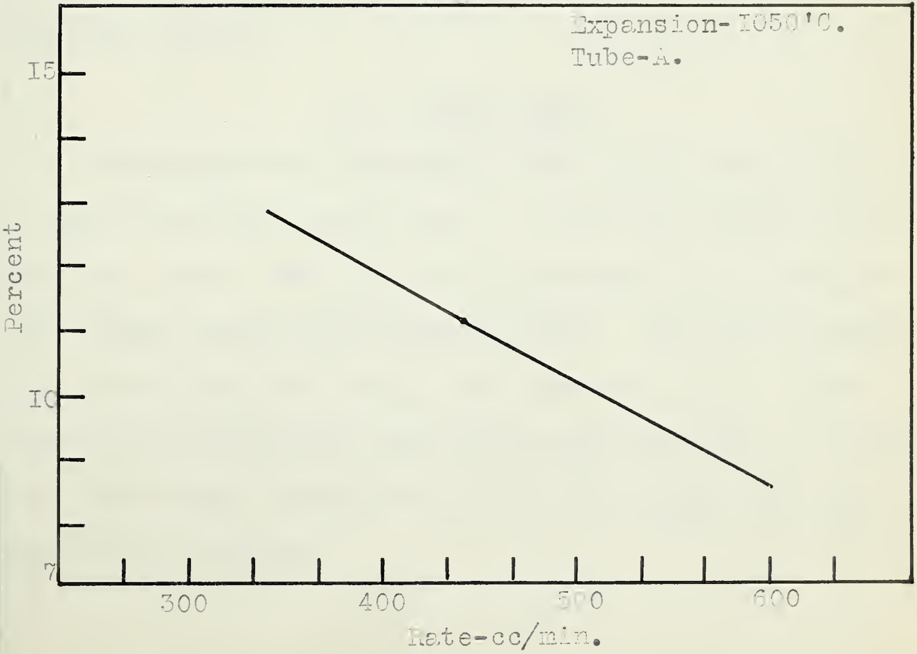

Hydrogen-I050'C.
Tube-A.
36
30
20
Percent
300
400
500
600
Rate-cc/min.

Fig.20


Expansion-I050'C.
Tube-A.
15
10
7
Percent
300
400
500
600
Rate-cc/min.

true oil yield. The other four runs are shorter and therefore errors of 2% or more due to gas adsorption may be included in these yields.

4. 2-cm. Tube

A complete survey of the behavior of Viking gas for temperatures of 950°C, 1000°C, 1050°C and 1100°C was made with a 2-cm. quartz tube in a 14 cm. furnace. This tube is illustrated in Plate II. Volumes of gas used in each case exceeded 100 litres and in some cases were several times that amount. The yields therefore presented in Table V, P. 70, closely approximate the recoverable oil yield. In this work, however, oil yield was calculated on weight increase of the absorption train. See Fig. 21-35.

5. 7-mm. Tube

Viking gas was studied at 1050, 1100 and 1150°C. in a 7-mm. straight quartz tube. A vertical furnace 15 cm. long was used. The core of the furnace was an alundum tube wound evenly with nichrome wire. The heat insulation about the core was in the form of a cone. Thus there was considerable heat loss near the apex. In this way the maximum temperature zone was brought near the base of the furnace.

TABLE V.

2 cm. TUBE

Run	Temp.	Rate of Flow	Time in Furnace	Volume of Gas	Expansion	Unsaturateds	H_2	CH_4	Oil Yield		
#		cc/mm	Sec.	Litres	%	%	%	%	Gms.	%	Gals/ 1000 c.ft.
135	950	114	19.8	312	8.5	2.3	-	77.2	15.16	9.6	0.33
143		155	14.6	230	-	2.9	16.6	73.6	12.27	9.5	0.33
144		166	13.6	268	9.6	2.9	15.2	74.8	11.95	8.8	0.31
145		225	10.0	240	8.5	3.2	12.9	73.8	9.26	7.6	0.26
146	1000	215	10.5	310	12.1	-	-	-	13.85	11.6	0.40
147		332	6.82	156	11.3	3.1	19.6	70.0	9.35	12.0	0.42
148		460	4.89	314	-	2.9	16.9	71.2	14.19	9.0	0.31
149		420	5.38	298	10.3	3.2	18.6	71.5	13.85	10.4	0.36
150		260	8.70	157	11.5	2.7	20.4	70.2	9.60	12.0	0.43
151	1050	430	5.27	214	-	3.5	28.2	58.2	15.05	14.0	0.49
152		650	4.48	128	-	-	-	-	7.16	11.1	0.39
153		650	4.48	310	12.0	3.7	25.7	63.6	16.68	10.8	0.37
154		815	2.78	710	8.5	3.9	15.4	71.0	26.33	7.4	0.26
155		420	5.38	228	14.2	3.1	20.0	-	14.90	12.95	0.45
156		382	5.92	195	12.7	2.9	27.5	-	12.03	12.5	0.44
157	1100	860	2.63	380	10.3	3.6	26.9	62.4	17.06	8.9	0.30
158		520	4.35	163	-	3.4	29.2	60.3	9.75	11.9	0.41
159		853	2.65	180	13.6	3.6	24.5	64.2	8.95	9.9	0.40
160		965	2.35	-	11.5	3.7	17.0	73.0	-	-	-

Fig.21

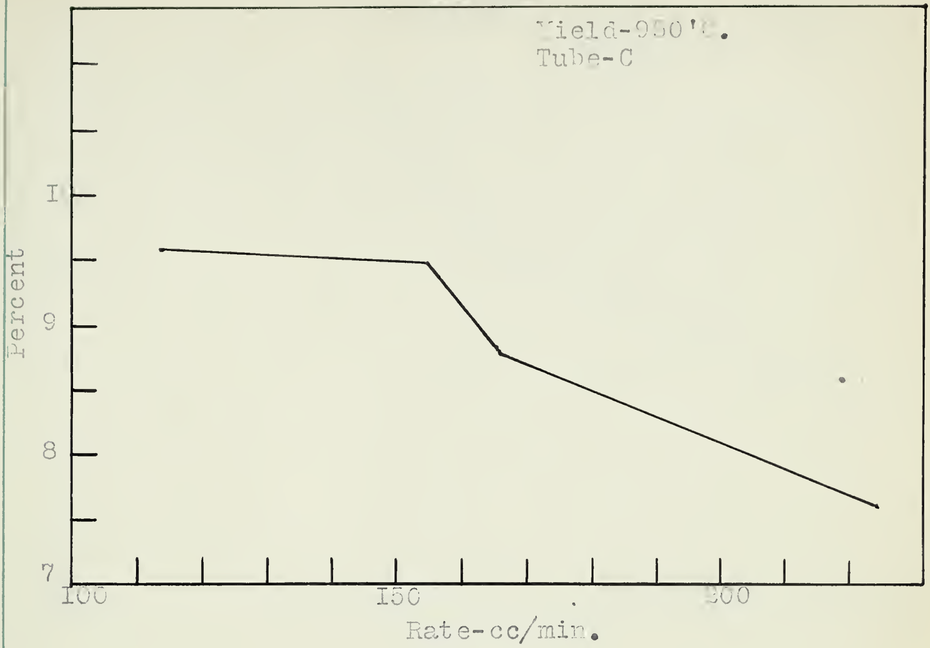

Yield-950'C.
Tube-C
Percent
10
9
8
7
100
150
200
Rate-cc/min.

Fig.22

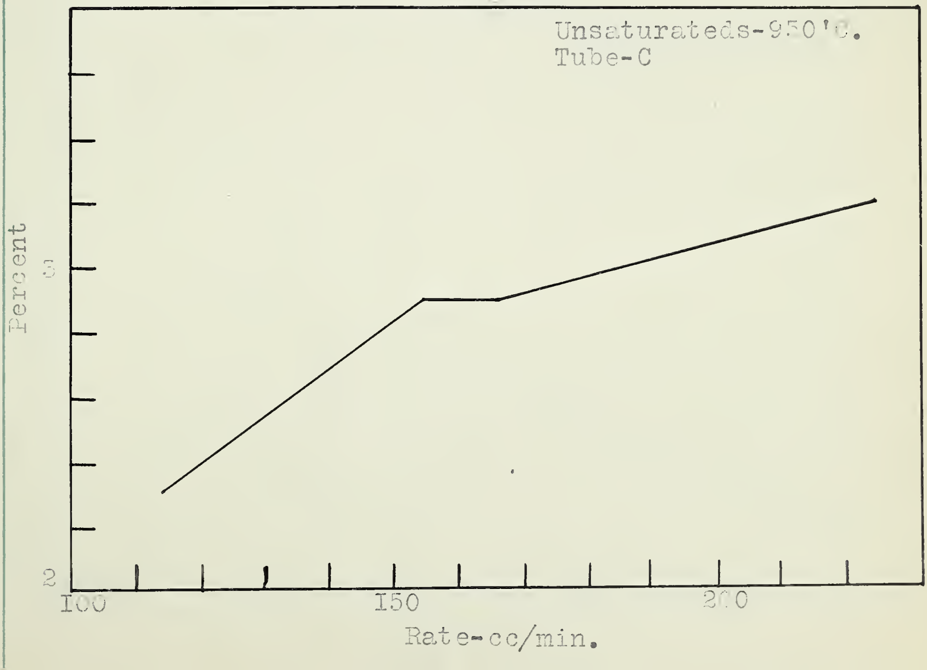

Unsaturateds-950'C.
Tube-C
Percent
3
2
100
150
200
Rate-cc/min.

Fig.23

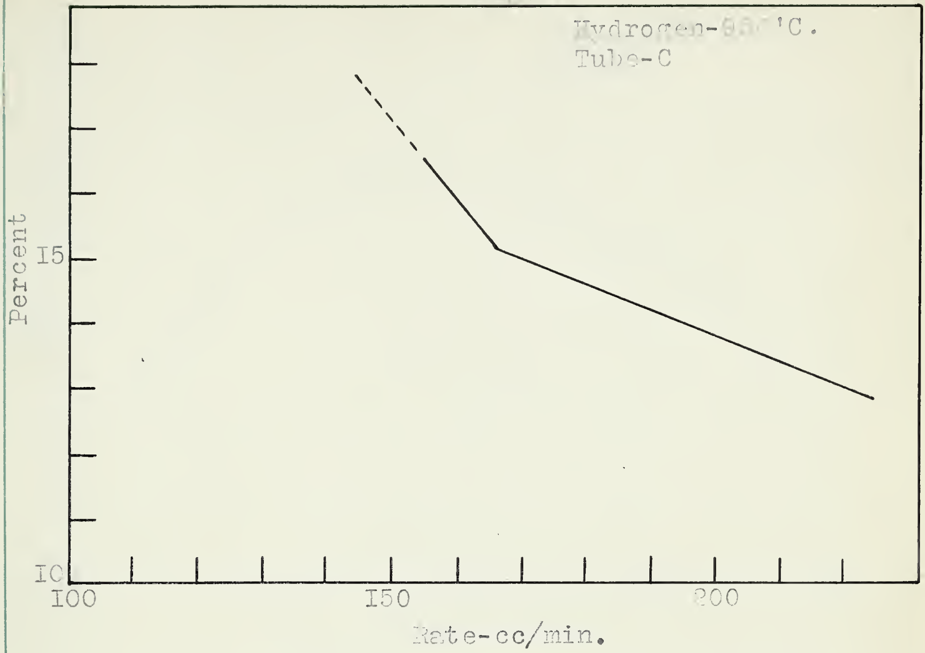

Hydrogen-950'C.
Tube-C
Percent
15
10
100
150
200
Rate-cc/min.

Fig.24

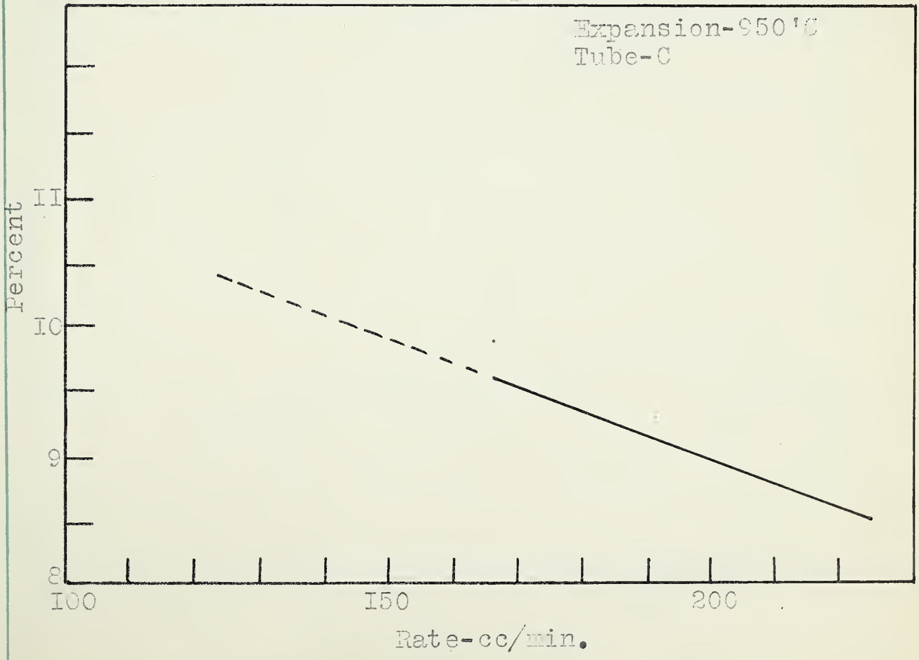

Expansion-950'C
Tube-C
Percent
11
10
9
8
100
150
200
Rate-cc/min.

Fig.25

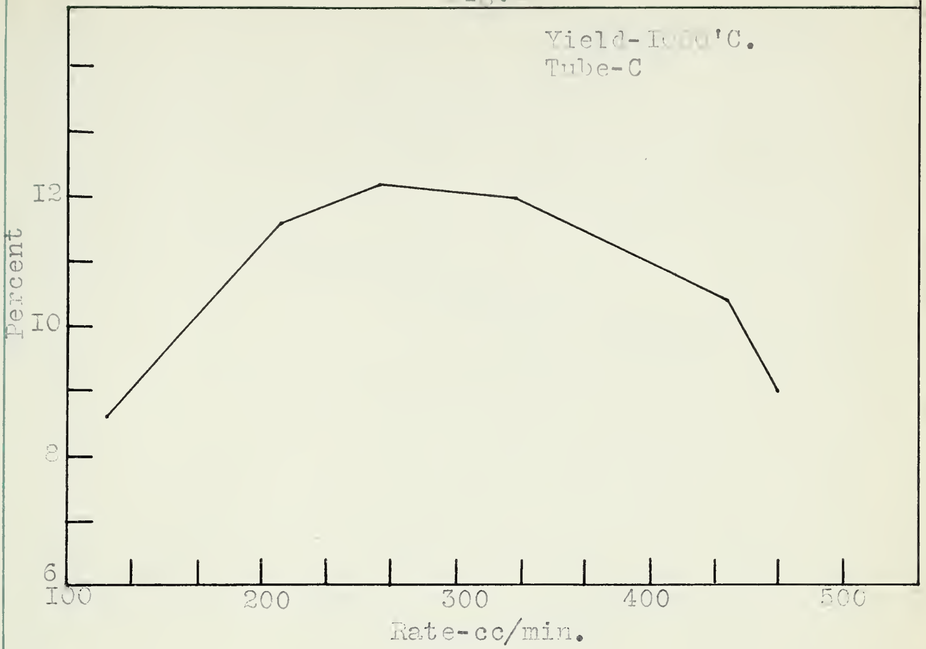

Yield-1000'C.
Tube-C
Percent
12
10
8
6
100
200
300
400
500
Rate-cc/min.

Fig.26

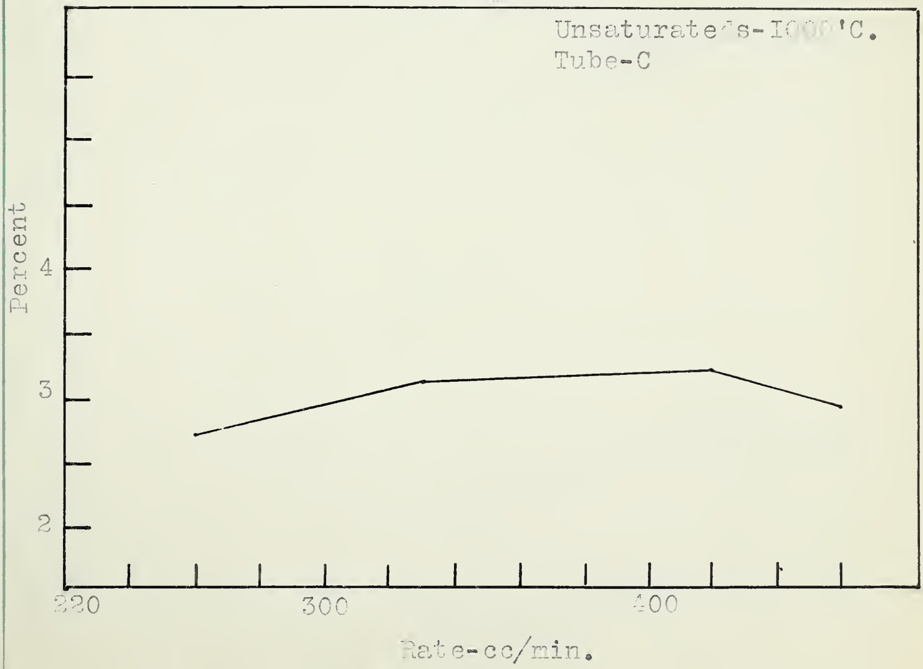

Unsaturated's-1000'C.
Tube-C
Percent
4
3
2
220
300
400
Rate-cc/min.

Fig.27

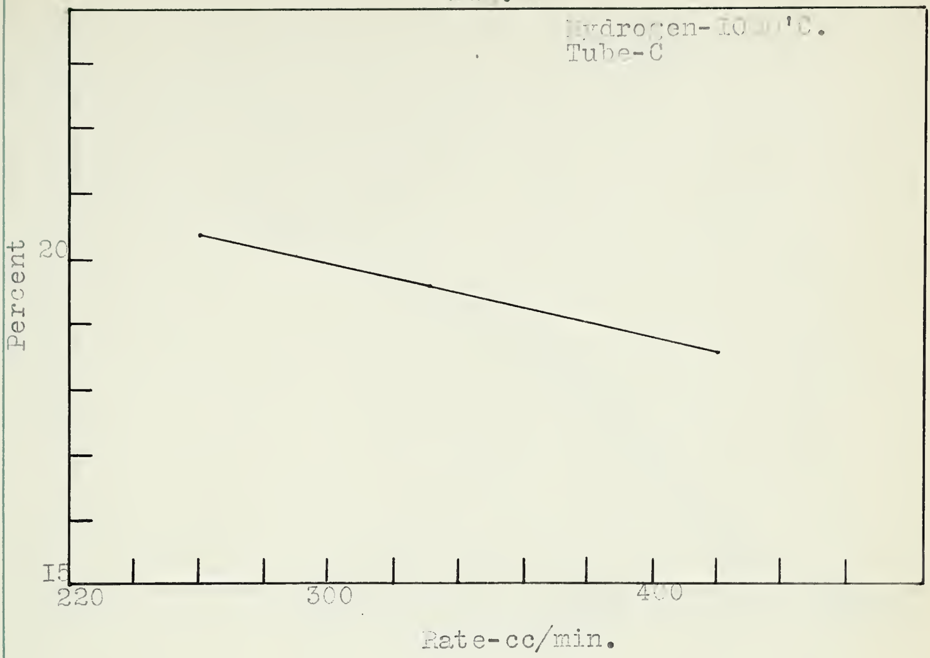

Hydrogen-I000'C.
Tube-C
Percent
20
I5
220
300
400
Rate-cc/min.

Fig.28

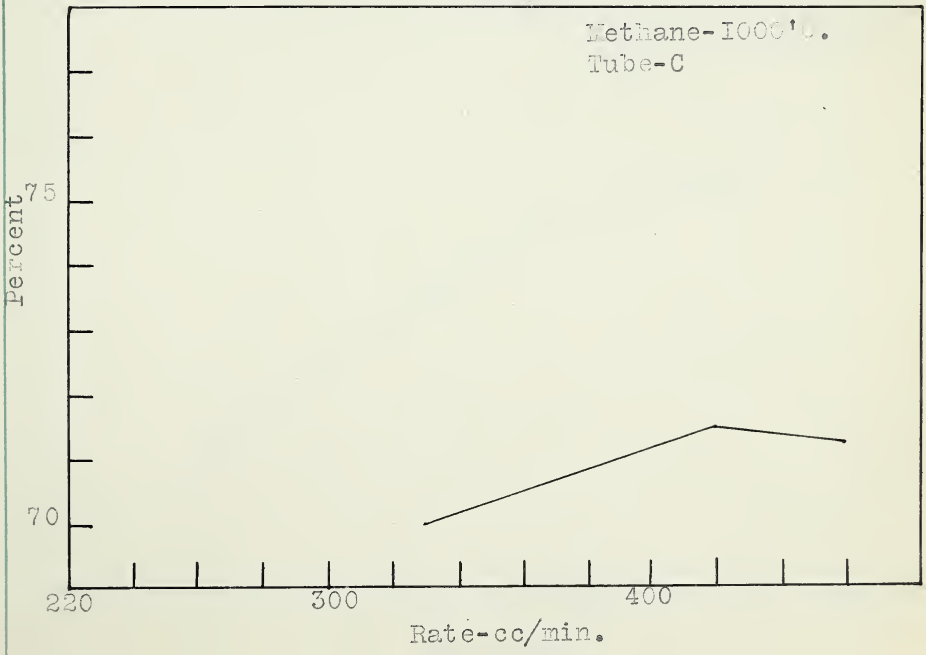

Methane-I000'C.
Tube-C
Percent
75
70
220
300
400
Rate-cc/min.

Fig.29

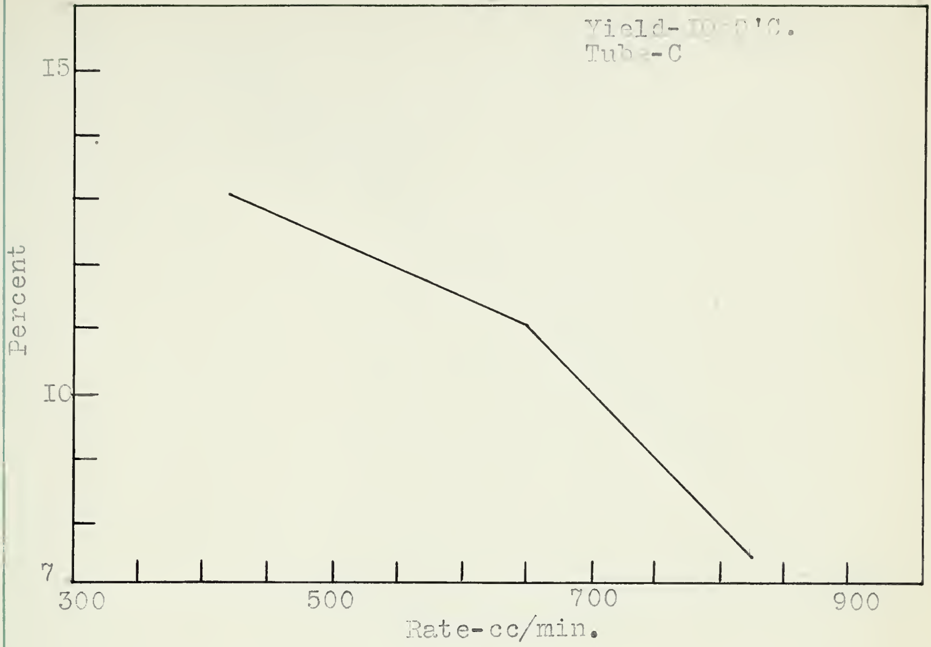

Yield-IO50'C.
Tube-C
I5
IO
7
Percent
300
500
700
900
Rate-cc/min.

Fig.30

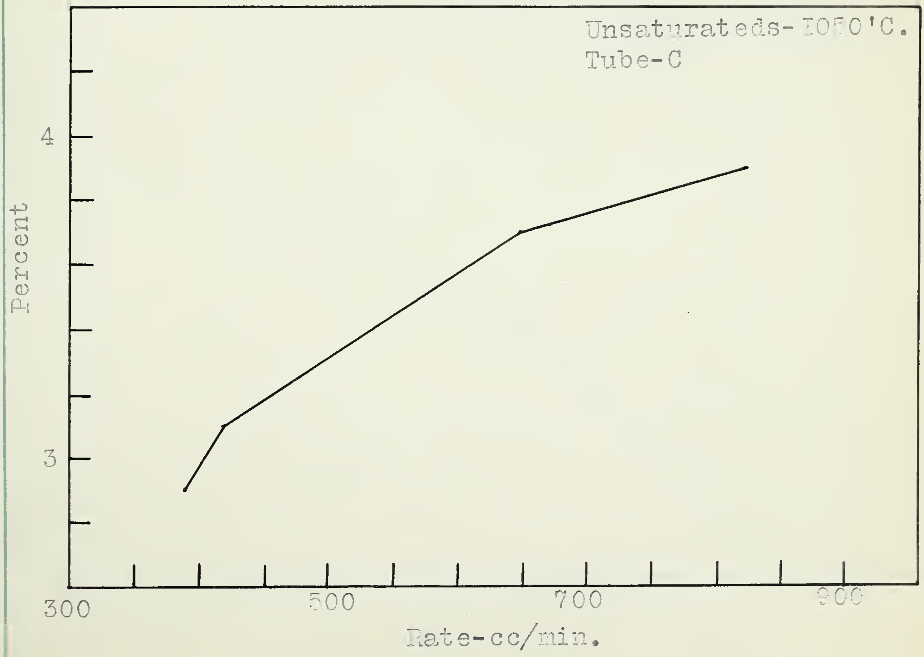

Unsaturateds-IO50'C.
Tube-C
4
3
Percent
300
500
700
900
Rate-cc/min.

Fig.31

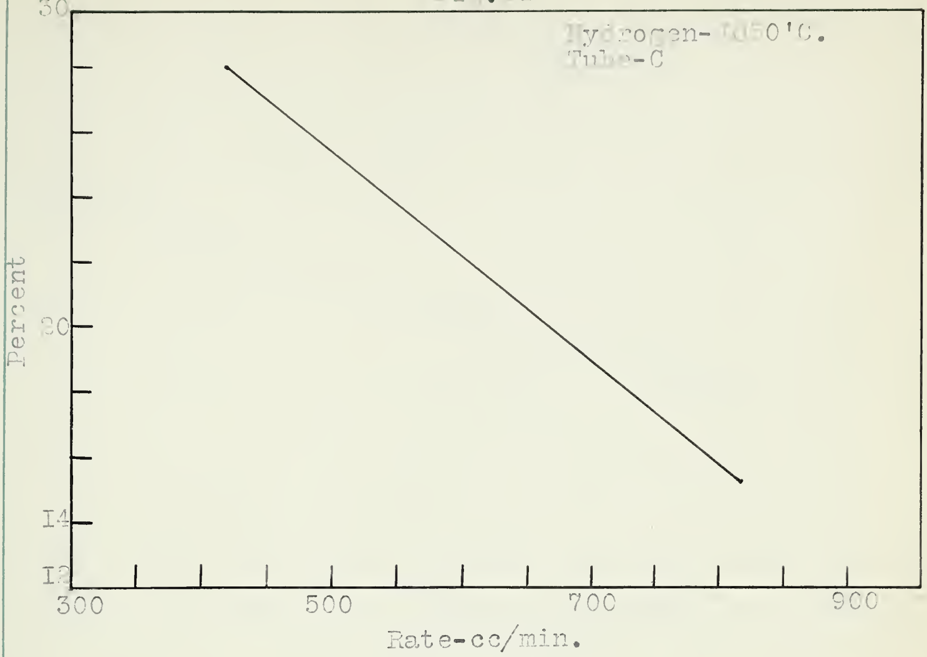

Hydrogen-1050'C.
Tube-C
Percent
30
20
14
12
300
500
700
900
Rate-cc/min.

Fig.32

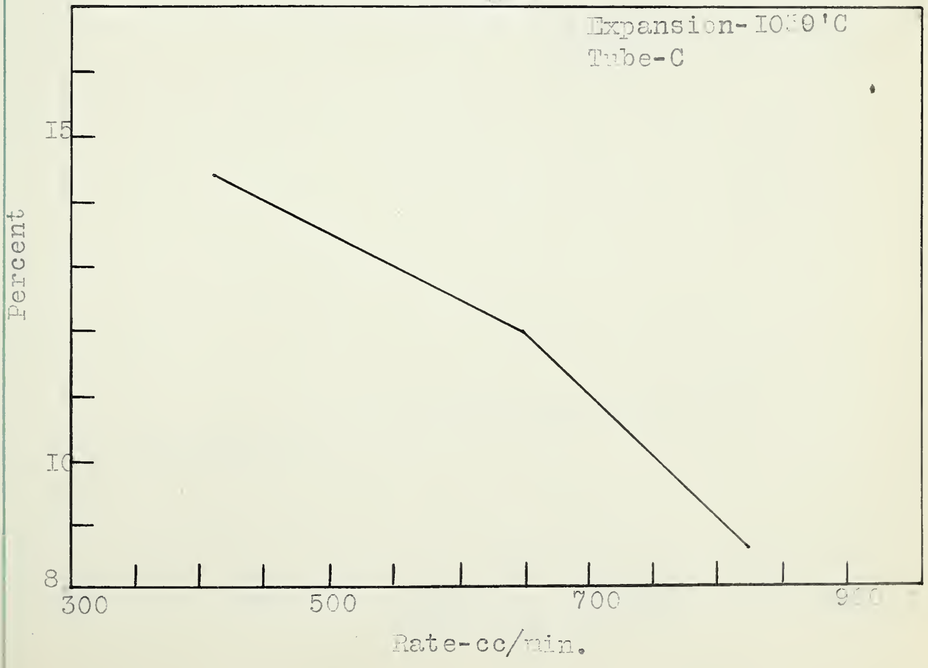

Expansion-I059'C
Tube-C
Percent
15
10
8
300
500
700
900
Rate-cc/min.

Fig.33

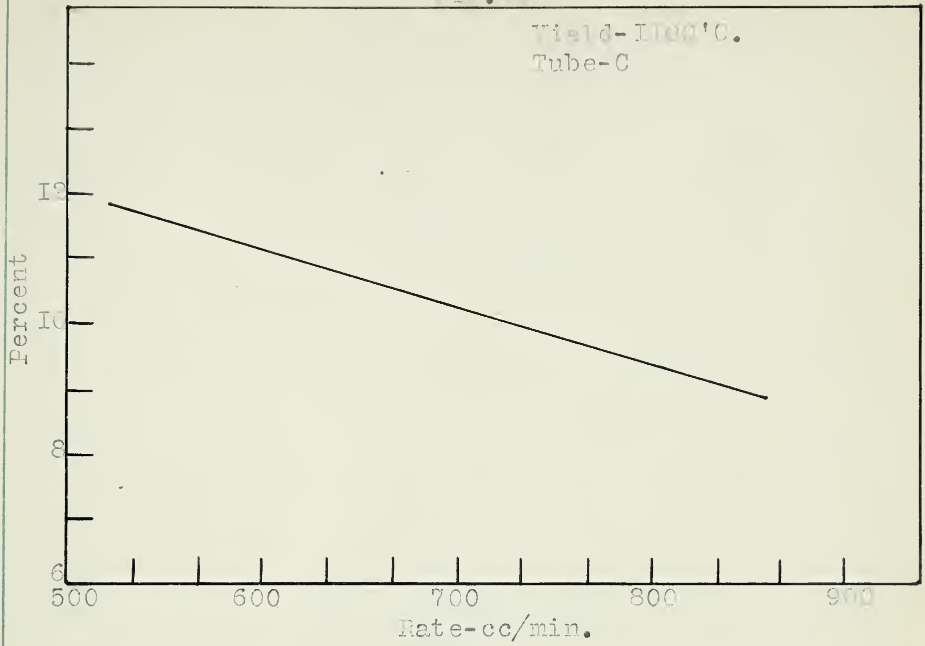

Yield-II00'C.
Tube-C
Percent
I2
I0
8
6
500
600
700
800
900
Rate-cc/min.

Fig.34

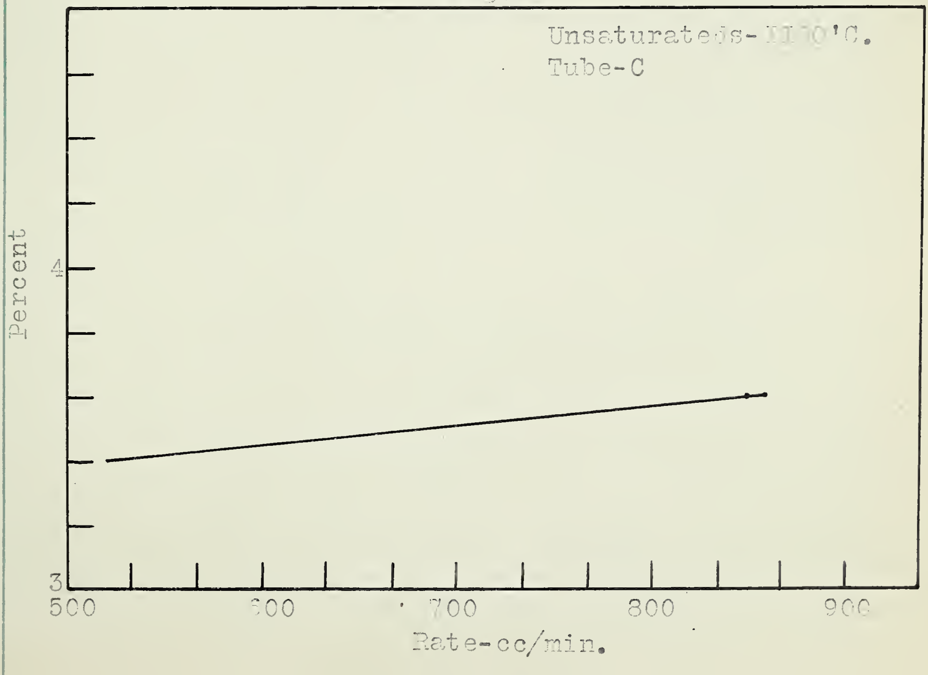
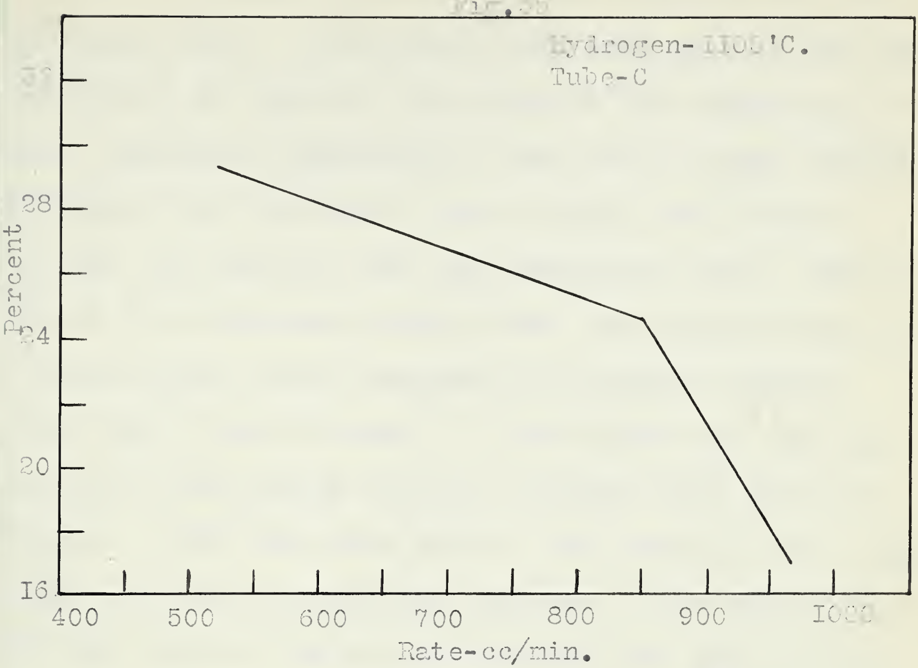

Unsaturateds-II00'C.
Tube-C
Percent
4
3
500
600
700
800
900
Rate-cc/min.

Fig.35


Hydrogen-II05'C.
Tube-C
32
28
24
20
I6
Percent
400
500
600
700
800
900
I000
Rate-cc/min.

The procedure differed somewhat from that in the preceding work. It had been found that most of the gas absorption by charcoal took place at the beginning of a run. Instead of depending on long runs to give reliable results, it was decided to pass a cubic foot of gas through the reaction tube and absorption train, then to remove the condensers, weigh them, and replace them for a second step, which consisted in passing a second cubic foot of gas through. It was found that the true values for oil yields could be obtained with this procedure. A few runs were made in this manner, but it was found difficult to duplicate results. This was due to the fact that at the end of each step the gas had been turned off. The gas in the furnace during this time was therefore given a long severe heat treatment which caused the production of soft carbon, which hindered oil formation. In succeeding runs the gas flow was continued during weighings, and thus uniform conditions were maintained in the furnace.

It was found possible to explore an entire temperature range in one run by varying the rates for each step. It was also found that by saturating the charcoal with natural gas before a run was made, excessive yields in the first step were avoided. Apparently as the unsaturated gaseous products were absorbed by the

TABLE VI

0.7 cm. TUBE

Run	Temp.	Vol.	Rate	Time in Furnace	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Total Oil	Yield
#	%	c.ft.	cc/mm	Sec.	%	%	%	%	G.	G.	G.	%
192-1	1050	1	92	3.76	5.6	-	-	--	0.91	1.89	2.80	22.4
2			92	3.76	9.6	3.2	19.4	68.0	0.78	0.91	1.69	11.9
3			84	4.13	10.4	3.5	23.2	64.3	0.86	0.67	1.53	10.8
4			86.5	4.01	10.0	3.2	25.8	62.6	0.91	0.81	1.72	12.2
5			88.5	3.92	10.6	3.4	21.5	66.8	1.03	0.63	1.66	11.3
6			83.2	4.17	-	3.55	25.0	60.0	0.67	0.71	1.38	9.7
7			119	2.91	10.5	-	-	-	0.56	0.65	1.21	8.5
8			125	2.77	10.7	3.5	19.3	67.3	0.41	0.77	1.18	8.4
9			142	2.44	-	3.3	16.3	68.3	0.57	0.69	1.26	10.3
193-1	1100	1	141	2.46	10.6	3.6	22.5	65.0	0.76	1.28	2.04	14.3
2			115	3.01	12.3	4.2	25.4	62.6	0.93	0.90	1.83	12.9
3			141	2.46	-	3.5	21.6	66.3	0.59	0.91	1.50	12.3
4			156	2.22	11.3	3.6	20.0	-	0.70	0.44	1.14	10.2
5			106	3.27	13.8	3.8	25.1	64.0	0.91	0.78	1.69	11.8
6			76.6	4.52	16.6	3.5	29.4	60.2	1.02	0.81	1.83	12.8
7			113	2.60	13.6	3.6	24.4	64.2	0.70	0.88	1.58	11.1
8			170	2.04	-	-	-	-	0.46	0.60	1.06	7.6
195-1	1150	1	324	1.07	20.7	4.0	32.8	-	0.93	0.83	1.76	12.3
2		1	316	1.10	20.1	3.9	33.0	-	1.27	1.02	2.29	16.3
3			324	1.07	20.3	3.8	30.3	-	0.82	1.38	2.20	15.5
4			338	1.02	18.3	4.4	31.0	-	0.81	1.12	1.93	13.5
5			326	1.06	18.2	4.0	28.4	-	0.61	1.21	1.82	13.4

Fig. 36

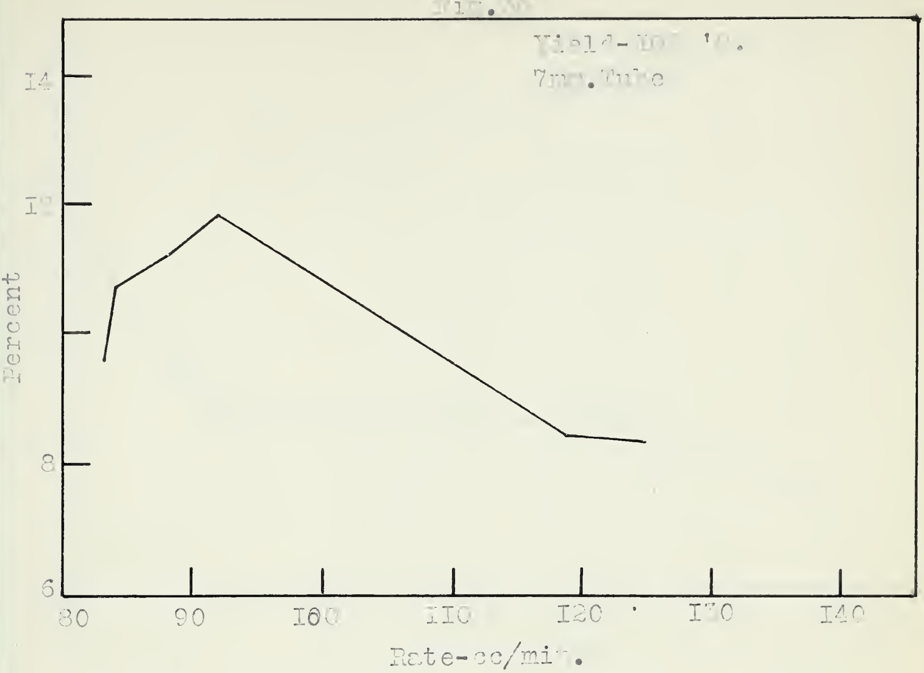

Yield-I050'C.
7mm.Tube
Percent
I4
I2
8
6
80
90
I00
II0
I20
I30
I40
Rate-cc/min.

Fig. 37

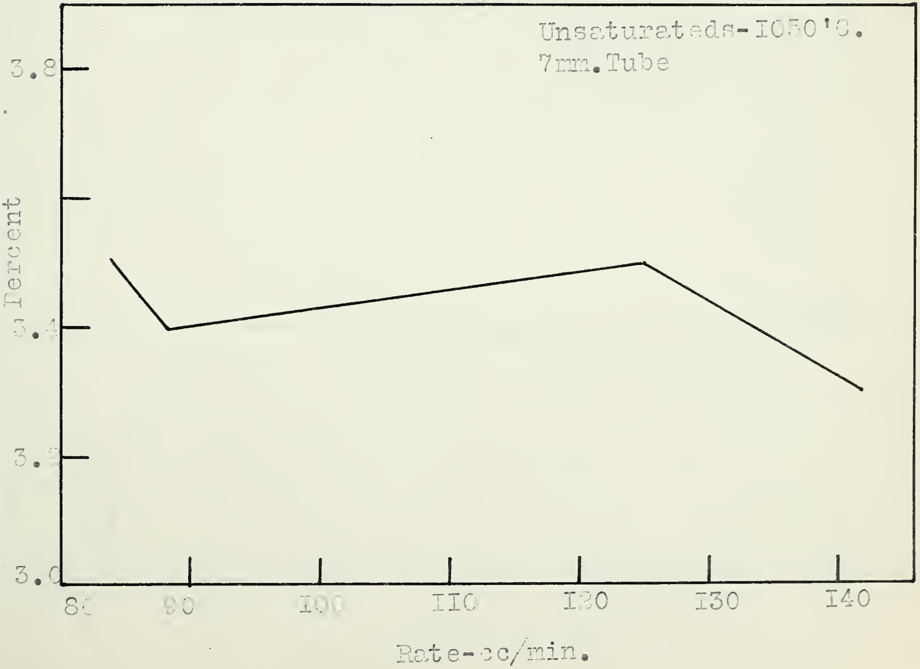

Unsaturateds-I050'C.
7mm.Tube
Percent
3.8
3.4
3.2
3.0
80
90
I00
II0
I20
I30
I40
Rate-cc/min.

Fig.38

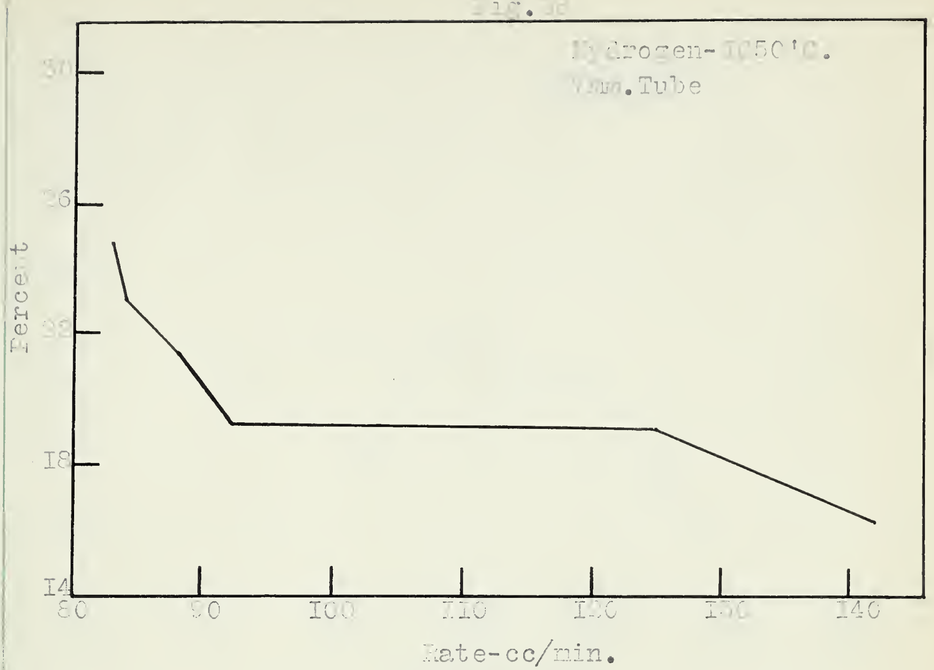

Hydrogen-I050'C.
7mm.Tube
Percent
30
26
22
I8
I4
80
90
I00
II0
I20
I30
I40
Rate-cc/min.

Fig.39

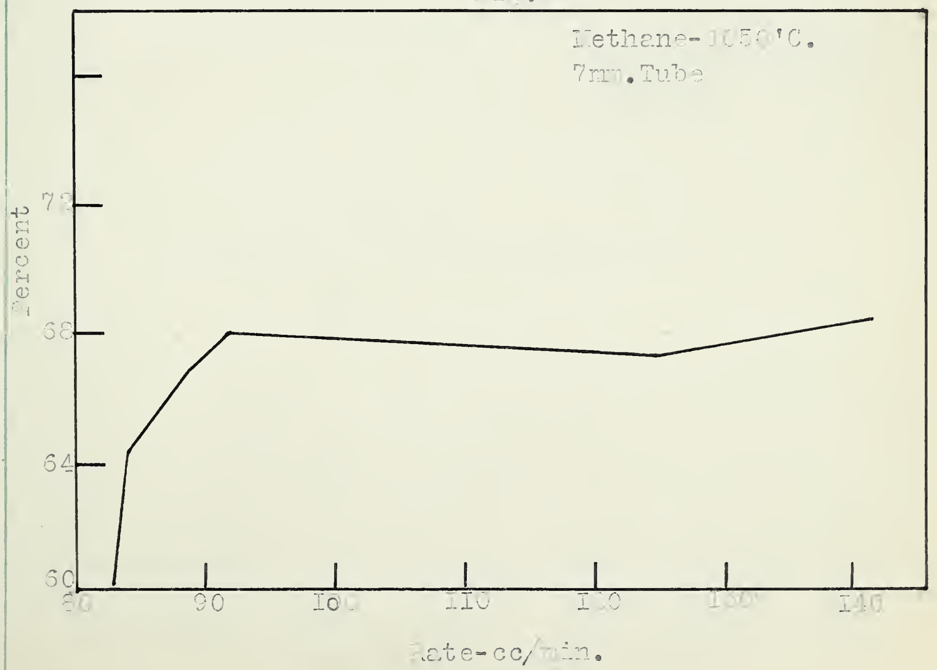

Methane-I050'C.
7mm.Tube
Percent
72
68
64
60
80
90
I00
II0
I20
I30
I40
Rate-cc/min.

Fig.40

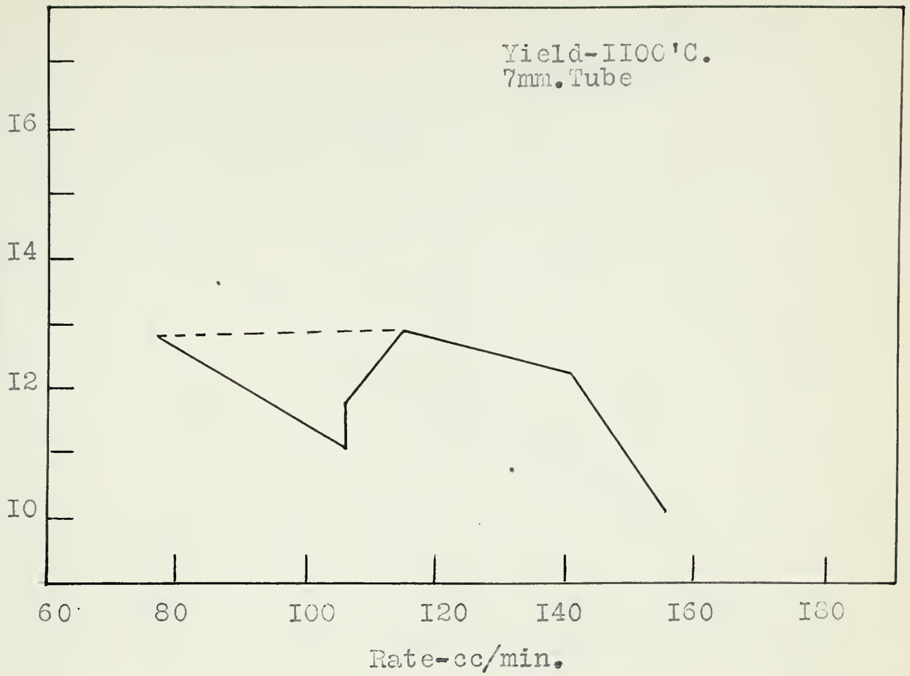

Yield-IIOO'C.
7mm.Tube
I6
I4
I2
IO
60
80
IOO
I20
I40
I60
I80
Rate-cc/min.

Fig.4I

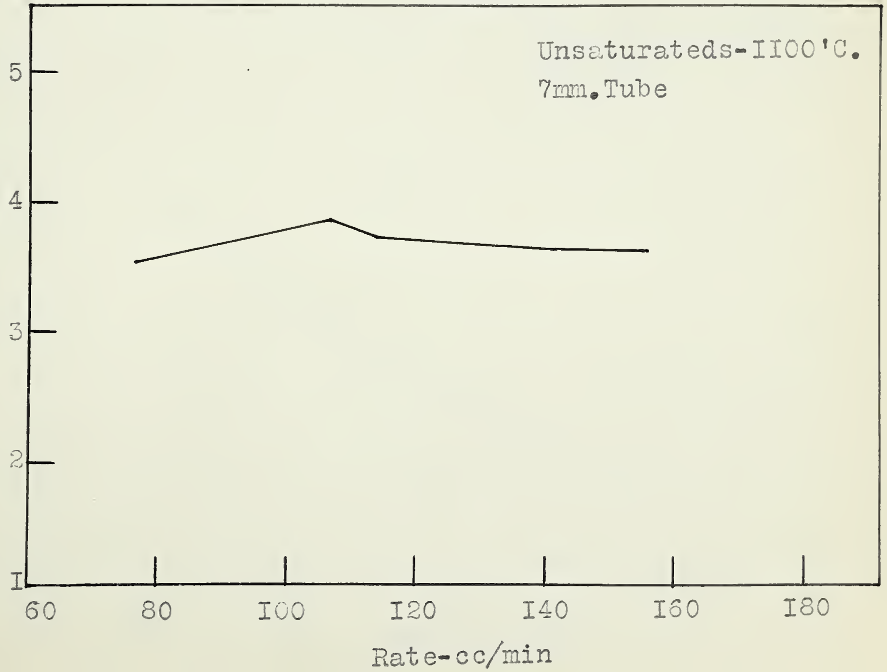

Unsaturateds-IIOO'C.
7mm.Tube
5
4
3
2
I
60
80
IOO
I20
I40
I60
I80
Rate-cc/min

Fig.42

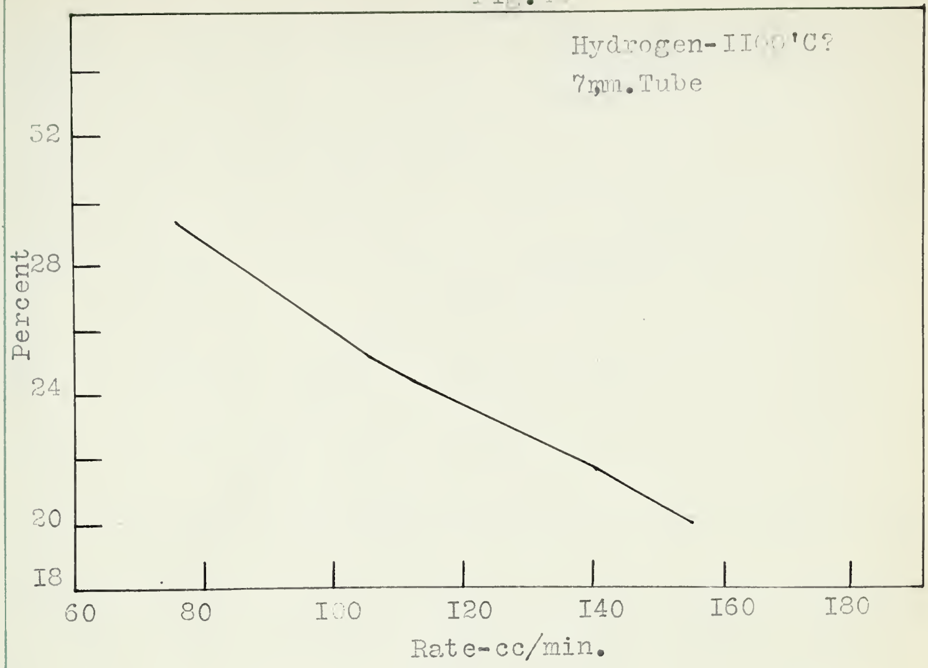

Hydrogen-II00'C?
7mm.Tube
Percent
32
28
24
20
I8
60
80
I00
I20
I40
I60
I80
Rate-cc/min.

Fig.43

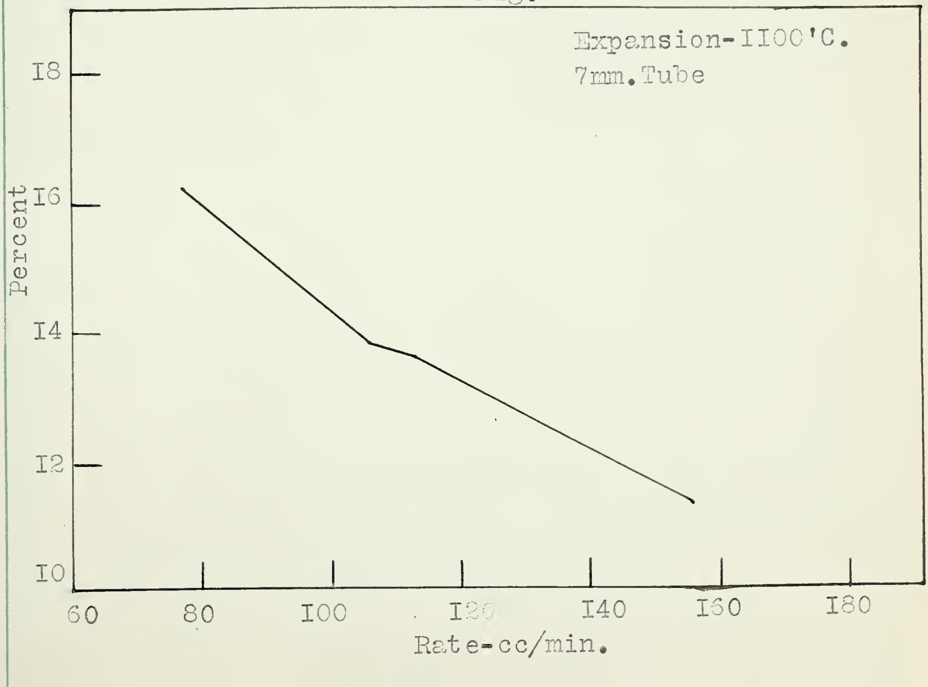
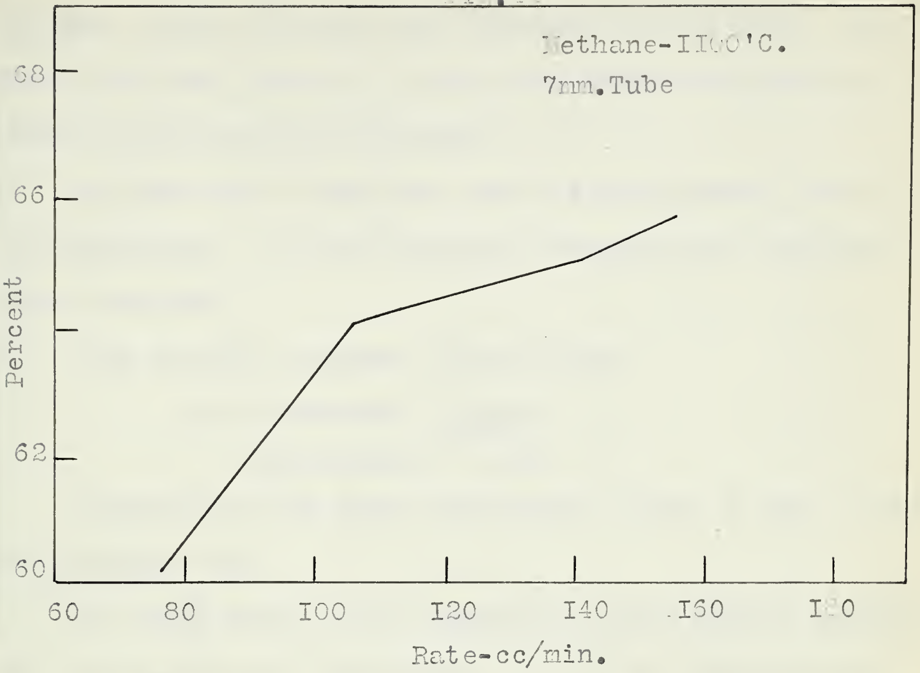

Expansion-II00'C.
7mm.Tube
Percent
I8
I6
I4
I2
I0
60
80
I00
I20
I40
I60
I80
Rate-cc/min.

Fig.44


Methane-II00'C.
7mm.Tube
68
66
62
60
Percent
60
80
I00
I20
I40
I60
I80
Rate-cc/min.

charcoal an approximately equal weight of methane was displaced. This procedure was followed in run #195. In run #193 and 194, Table VI, P. 80, the steps are given in the order in which they were made.

At the end of each run the oil was steamed out of the charcoal. A 94.6% total oil recovery was obtained from run #192.

The weight increase = 14.43 grams
Oil recovered = 13.67 "
Difference .76 "

Therefore 0.76 grams consisted either of gas or non-recoverable oil.

In 192-1 there is an abnormally large weight increase in the charcoal of 1.89 grams. If it is assumed that the 0.76 grams not recovered is due to gas adsorption in the first step, then the percentage yields in run #192 represent the oil actually recovered.

In run #193 the recovery was only 88% of the weight increase. This low recovery is difficult to explain. In run #195 the yield recovered amounted to 12.2%, or 0.43 gallons per 1000 cu. ft. The results are shown in Fig. 36-44.

6. Circulation Experiments

In the work on the pyrolysis of Viking gas it was found that the residual gas still contained from 60 to 80% undecomposed methane. The other constituents of the

gas consisted of approximately 3% unsaturated hydrocarbons, and from 10 to 30% hydrogen. The small percentage of nitrogen in the original gas came through the reaction unchanged. The possibility of obtaining more oil from the residual gas by passing it through a second furnace seemed plausible. Wheeler and Wood (28) state that with a concentration of less than 60% methane no oil can be produced.

Two sets of runs were made in order to determine whether oil could be produced from a gas low in methane content.

Viking gas was passed through the usual apparatus which in this case consisted of a flow meter, gas meter, and reaction tube, with an absorption train consisting of a trap, electrical precipitator, and one charcoal condenser. A second gas meter followed the charcoal condenser.

The temperature of the furnace was 1050°C. and the rate was adjusted to produce a maximum yield. The conditions for maximum yield could be fairly closely judged by observing the nature of the tar fog. Dense rich cream (almost light brown) fumes indicated a high oil concentration in the residual gas. Slightly higher yields were obtained from light brown fumes, but they indicated carbon formation , which was undesirable, as it ultimately plugged the reaction tube.

TABLE VII

CIRCULATION EXPERIMENTS - VIKING GAS

Run	Rate	Time in Furnace	Vol. of Gas	Temp.	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Yield	Conversion $CH_4 \rightarrow$ Oil
#	cc/mm	Sec.	Litres	°C.	%	%	%	%	Gms.	Gms.	%	%
187												
A	392	3.5	235	1050	13.5	3.3	24.1	63.8	7.08	7.86	12.7	45.8
B	445	3.08	266	1120	6.9	3.8	42.6	45.7	5.98	7.45	11.4	64
C	250	5.5	183	1050	2.0	2.6	48.1	40.6	1.56	3.50	5.5	118
D	257	5.33	195	1127	4.6	2.7	55.2	33.0	1.53	3.10	5.0	78
							Totals		16.15	21.91	34.6	
188												
A	623	2.2	301.5	1050	9.4	3.6	16.6	71.2	3.93	8.01	7.9	36
B	682	2.01	330.0	1110	9.3	3.7	29.8	57.0	3.46	5.80	6.7	63.4
C	342	4.00	201.0	1050	1.8	3.8	36.4	50.3	2.35	4.39	6.7	112
D	349	3.93	214.0	1130	6.4	3.6	50.2	36.5	2.85	4.65	7.9	59.5
							Totals		11.59	22.85	29.2	

The residual gas, after it was stripped of its oil, was passed directly through a second similar reaction tube and condenser system. The rate was higher due to an expansion of 13.5% in the first tube. The temperature of the second furnace had to be raised to accommodate this increase in rate since it was desired to obtain the densest fumes possible in the second step. The gas entering the second reaction tube contained 24.1% hydrogen. According to Fischer a diluent necessitates a rise in temperature to produce the same corresponding yield. In order to obtain the richest fog it was found necessary to raise the temperature of the second furnace to 1120°C. The fog produced appeared to be as dense as that from reaction tube #1, and on calculating the yield it was found almost as high. See Table VII, P. 88. The yields given were not corrected for gas adsorption, but serve for comparative purposes.

The gas from the second furnace was run into a gas holder. This gas was then run through two more similar furnaces in order to determine just how far this process could be carried. The temperatures were respectively 1050 and 1127°C.

In the above experiment temperatures and rates were so adjusted that the maximum possible yield was obtained at each step. It was desired to study the behavior of

the gas under less rigorous temperature conditions. A second experiment was performed with this object in view.

The first furnace was kept at 1050°C., but the rate was 623 cc. per minute instead of 392, as in the former experiment. The fumes were therefore kept almost white but they were quite dense. This resulted in the low yield of 7.9%. The second furnace was kept at 1110°C. as these conditions appeared to give fumes identical with those from furnace #1. The calculated yield, however, proved to be lower; i.e., 6.7%. In furnace #3 the fumes were approximately the same as in #1 and 2, and the yield was 6.7%. As furnace #4 furnished the last step, an attempt was made to get as much oil as possible. With the furnace at 1130°C. the fumes were a rich cream and were fairly dense. The yield rose to 7.9%.

Several interesting features permit of discussion:

1. By cracking in four steps the yield has been trebled.
2. With strenuous cracking conditions, as in run #187, Table VII, the tar/light oil ratio = 0.74. In run #188, with less strenuous cracking conditions, the tar fraction is considerably lower, the ratio being 0.52. In a one step run the ratio is approximately 1.0. This therefore suggests a simple method of obtaining a larger yield of light oil at the expense of the less desired tar.

A more detailed discussion will be given on the work with Turner Valley gas.

3. It was found that oil was still produced in considerable quantity after the methane concentration had fallen below 40%. This is a contradiction of the work of Wheeler and Wood.

4. In run #187, 36.2% methane was decomposed in the first step, 18.1% in the second, 5.1 in the third and 7.6 in the fourth. It is of interest to know what percentage of this is converted to oil, and to determine how much is completely decomposed to carbon and hydrogen.

Tar formation makes it difficult to make an accurate determination, but approximate results can be obtained.

No large error is introduced by representing the entire reaction by the two following equations:

$$\begin{array}{l} 6CH_4 \longrightarrow C_6H_6 + 9H_2 \\ 10CH_4 \longrightarrow C_{10}H_8 + 16H_2 \\ \hline 16CH_4 \longrightarrow 25H_2 \\ 1CH_4 \longrightarrow 1.56H_2 \end{array}$$

A yield of 12.7% should result in the production of 19.8% H_2. In step 1, 24.1% H_2 was produced. This indicates that 4.3% H_2 was produced by the reaction

$$CH_4 \longrightarrow C + 2H_2$$

Stanley and Nash (26) found that 9.7% of CH_4 decomposed directly to carbon and hydrogen, in the above reaction, at 1150°C. The work discussed here was at 1050°C. In the second step the excess H_2 is reduced to 0.7%. This is reflected in the large drop in expansion. In the third and fourth steps, the total hydrogen produced is somewhat less than that required for oil formation alone. The discrepancy, however, is not great. It may be concluded that direct decomposition of methane to carbon and hydrogen rapidly decreases as the hydrogen concentration increases.

5. The percentage conversion of methane to oil has been calculated and is included in the table. The conversion increases to a maximum and then decreases. The reason that it reaches more than 100% in step three is due to the fact that yields were calculated on weight increases, which are slightly higher than the true oil weight. The drop in percentage conversion in the fourth step is due to the fact that the gas in the final step was subjected to more strenuous thermal conditions than in the preceding step, in order to produce as high a yield as possible. The relative increase in hydrogen production indicates this.

7. Nitrogen Experiments

Fischer found that an inert gas such as nitrogen has no effect on the reacting gas except that it requires a rise in temperature to repeat yields obtained from pure methane. Nitrogen was therefore convenient to use in a study of the influence of the walls. Bone and Coward found that the decomposition of CH_4 to yield $C + H_2$ was a surface phenomenon. An attempt was made to determine what influence the surface of the reaction tube had on the production of oil. Wheeler and Wood found that by packing a quartz tube with pieces of broken quartz they obtained no increase in yield. However, this method so alters heat distribution and rate conditions that it is difficult to draw definite conclusions.

It was noted by Chamberlain and Bloom (6) that no oil fumes appeared in a clean tube until a definite amount of gas had been passed. The present work showed that approximately a tenth of a cubic foot had first to be passed through a clean tube before fumes appeared. The fumes were first pale, but rapidly deepened in color to a rich cream when appropriate rates were used. An examination of the tube after the experiment showed it to be coated with a thin foil-like pearl graphite. It was noted in one tube, after several runs had been made without cleaning the tube after each run, that there were

several distinct layers of this pearl graphite. The layers were less than 0.1 mm. thick and parted readily. This would indicate that in each run a separate layer of graphite was built up. In view of the small thickness of the layers, and since long use of a tube does not tend to choke it with graphitic carbon, it is doubtful whether this carbon building is a continuous process.

The reason for separate layers for each run can be explained. At the end of an experiment the gas flow is shut off, leaving a hot reaction tube in contact with the gas. It has been found by experiment that natural gas, when heated for a longer time than that required to produce oil, will produce a sooty carbon. The gas therefore at the end of each run will deposit a film of sooty carbon on top of the graphitic carbon. In a following experiment a fresh film of graphite must be deposited before the desired reactions commence.

In order to determine whether this graphite actually plays an active part in the formation of oil, the follow- comparative experiments were made.

In the one case N_2 was passed as a sheath along the walls of the reaction tube and tended to keep the methane in the centre of the tube. In the second case the nitrogen was passed through the centre of the tube, tending to force the methane against the walls.

The furnace and tubes used are illustrated in Plate III C. A long quartz tube, 1.5 cm. in diameter, was placed in a 6" furnace. A second tube, 7 mm. internal diameter, was placed coaxially with the first so that it projected 2" into the furnace. Gas could be passed through this into the larger tube. A rubber stopper and tube device allowed a second gas to enter at the upper end of the 1.5 cm. tube, and flow between the larger and smaller tubes. The 7 mm. tube ended where the high temperature zone of the furnace began. The nitrogen was passed down the outside tube, while the CH_4 passed through the 7 mm. tube. The N_2 and CH_4 mixed on coming in contact, but the rate of flow was fairly rapid, and the time in the furnace brief (See Table VIII, P. 96). The N_2 would therefore tend to protect the CH_4 from the wall and the yield should indicate the influence of the wall.

In each set of experiments a second run was made with the CH_4 passing down the outer tube, and the N_2 passing down the centre. In this case the CH_4 would be forced against the walls. A third run was made with CH_4 in both tubes. This acted as a check on yields.

Table VIII, P. 96 shows that CH_4, when forced against the walls of the tube, produced higher yields than the CH_4 protected from the effect of the walls. This would indicate that the pearl graphite acts as a catalyst in the

TABLE VIII

NITROGEN EXPERIMENTS

Run	Temp.	Rate Total	Rate CH_4	Time in Furn.	Vol. N_2	Vol. CH_4	Position of Gases	Expansion CH_4	Net Expansion	Unsat.	H_2	CH_4	N_2	Tar	Light Oil	Total	Yield
#	°C.	cc/ min.	cc/ min.	Sec.	L.	L.		%	%	%	%	%	%	Gms.	Gms.	Gms.	%
179	1050	409	409	3.08	0	261	CH_4 Inside & Outside.	12	12	3.3	20.4	66.5	8.1	6.35	9.23	15.58	11.9
180	1050	366	238	3.45	113	211	CH_4 Inside.	11.8	7.7	2.6	15.1	41.4	40.7	4.15	5.41	9.56	9.1
181	1050	365	218	3.46	129	183	CH_4 Outside.	13.5	7.9	2.3	14.3	39.8	41.0	5.23	6.01	11.24	12.2
182	1100	640	640	1.97	0	253	CH_4 Inside & Outside.	13.7	13.7	3.8	25.4	63.4	6.6	5.81	9.55	15.36	12.1
183	1100	627	337	2.02	220	261	CH_4 Inside.	11.8	6.4	2.3	13.1	37.1	53.1	5.32	9.81	15.13	11.5
185	1100	620	348	2.04	106	136.7	CH_4 Outside.	16.6	9.1	-	-	-	-	3.48	6.00	9.48	13.8

production of oil from gas by pyrolysis. The result is not absolutely conclusive as it is known that the temperature in the centre of the tube is below that at the walls. The presence of pearl graphite is essential, however, beyond any doubt. It is interesting to note that the presence of N_2 does not influence the percentage of unsaturated hydrocarbons in the gas referred to natural gas content.

B - Turner Valley Gas

Turner Valley gas which contained some sulfur was used in part of this work. It was found that the sulfur had no apparent influence on the oil yield, and no attempt was made to purify the gas. The apparatus used was the same as that used with the Viking gas. The gas was stored in high pressure gas cylinders. When a run was to be made the necessary amount of gas was run into a gas holder. The gas holder was then connected with a calcium chloride tower which in turn was connected to the pyrolysis apparatus. The condenser system consisted of a trap, electrical precipitator, and one charcoal condenser. The charcoal condenser was saturated with natural gas before an experiment was made. By doing this, it was found that there was no abnormally high weight increase during the passage of the first cubic foot of gas.

The reaction tubes used were 1.5 cm. and 0.7 cm. internal diameter, and consisted of quartz. A cone shaped furnace 15 cm. long was used. The temperature was measured by a Pt.-Pt.-Rd. thermocouple placed between the furnace and reaction tube. This thermocouple was calibrated against a second Pt.-Pt.-Rd. thermocouple which was placed in the hot zone of the reaction tube.

The composition of the gas used has been given in the introductory part of this paper. From this the weight of 22.4 litres of gas was found to be 18.0 grams. In calculating the percentage yield the gas was assumed to be methane with a molecular weight of 18.0 grams. The yield in gallons per 1000 cu. feet was calculated in the same manner as with Viking gas.

Each temperature was studied in a single run. The procedure followed was the same as that in section 5, where Viking gas was studied in a 7 mm. tube.

1. 1.5-cm. Tube

The 1.5 cm. tube was studied at temperatures of 950, 1000 and 1050°C. Table IX, P. 99, and Figs. 45-69, show the results. Tar and light oil yields are given in grams per cubic foot, for each step of the experiment, in order that they may be more readily compared. The total recoverable oil amounted to 95% of the yield as measured by weight increase.

TABLE IX

TURNER VALLEY GAS.

Run	Temp.	Vol.	Rate	Time in Furnace	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Total Oil	Yield	Yield
#	°C.	Cu.Ft.	cc/min	Sec.	%	%	%	%	Gms.	Gms.	Gms.	%	Gal./1000 c.ft.
200a	950	1	158	10.9	23.8	5.6	23.8	66.0	1.58	1.00	2.58	15.6	0.60
b			179	9.7	-	5.7	22.8	68.0	1.34	1.09	2.43	14.6	0.57
c			204	8.5	20.3	6.1		67.4	1.26	1.07	2.33	14.0	0.54
d			260	6.6	18.5	6.7	22.0	64.7	0.83	1.37	2.20	13.3	0.50
e			344	5.0		6.6	21.3	67.2	0.93	1.22	2.15	13.0	0.49
198a	1000	1	258	6.7	21.5	5.3	28.9	62.2	1.48	1.08	2.56	15.5	0.60
b			274	6.3	22.8	5.0	28.6	58.0	1.41	1.15	2.56	15.5	0.60
c			333	5.2	22.6	5.9	-	63.5	1.39	1.21	2.60	15.7	0.61
d			364	4.7	-	7.0	25.0	63.5	1.36	1.37	2.73	16.5	0.64
e			434	4.0	20.2	7.1	24.7	60.5	1.21	1.11	2.38	14.3	0.55
199a	1050	1	455	3.8	30.4	5.0	36.2	56.0	1.40	1.41	2.81	17.0	0.69
b			486	3.6	28.2	5.2	34.6	-	1.45	1.18	2.63	15.9	0.61
c			490	3.5	27.4	5.3	33.2	56.6	1.23	1.65	2.88	17.3	0.70
d			702	2.5	23.2	-	-	-	1.35	1.21	2.56	15.4	0.60
e			914	1.9	21.5	7.4	26.0	61.3	0.97	1.40	2.37	14.2	0.55

Fig.45

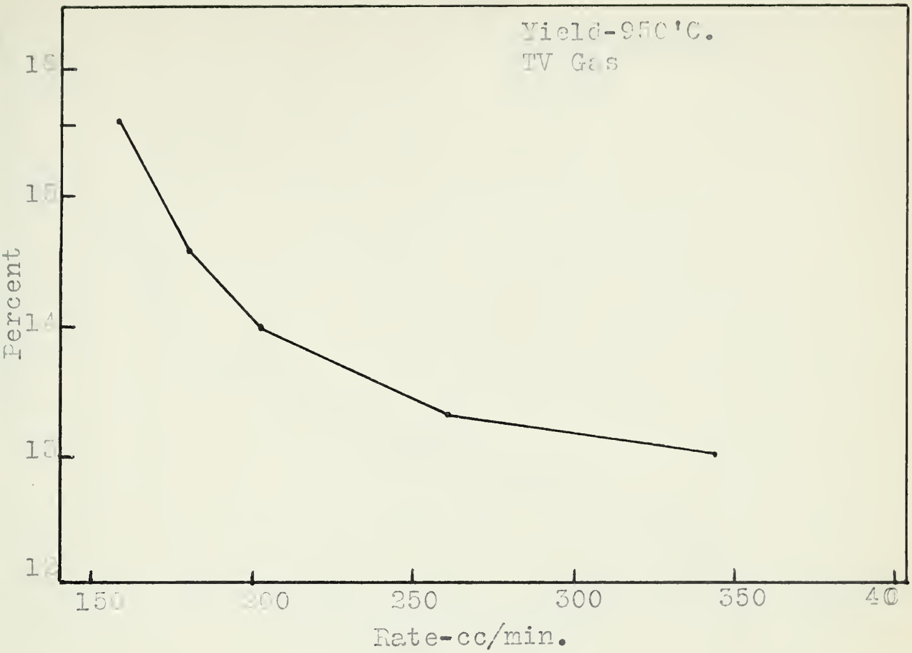

Yield-950'C.
TV Gas
16
15
14
13
12
Percent
150
200
250
300
350
400
Rate-cc/min.

Fig.46

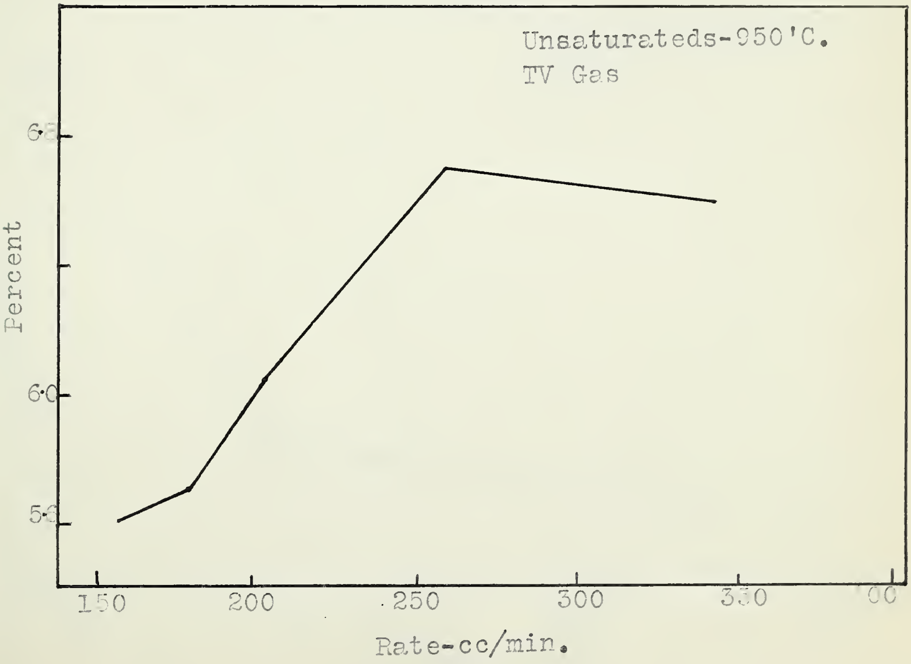

Unsaturateds-950'C.
TV Gas
6·8
6·0
5·6
Percent
150
200
250
300
350
400
Rate-cc/min.

Fig.47

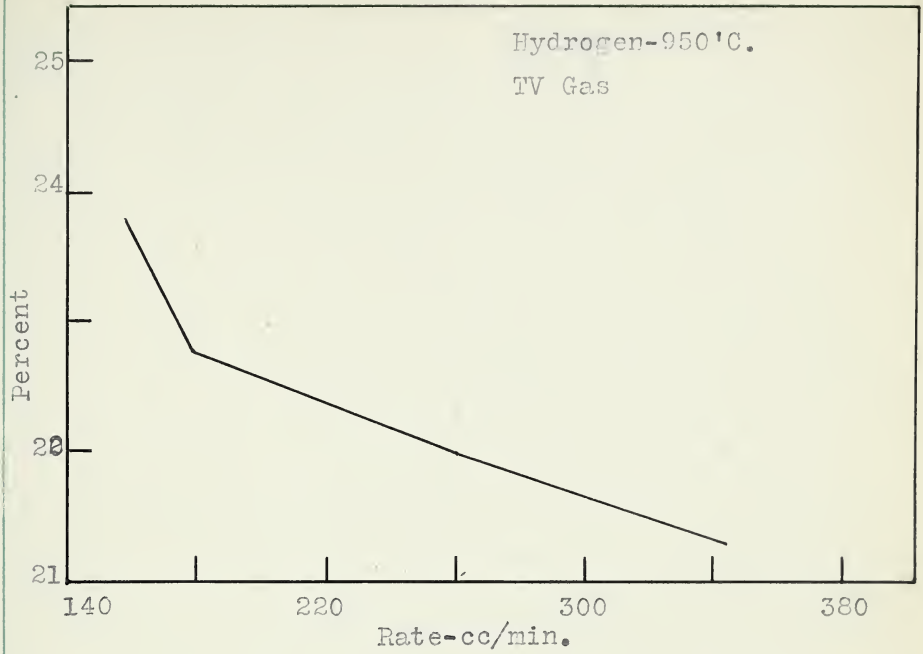

Hydrogen-950'C.
TV Gas
Percent
25
24
22
21
140
220
300
380
Rate-cc/min.

Fig.48

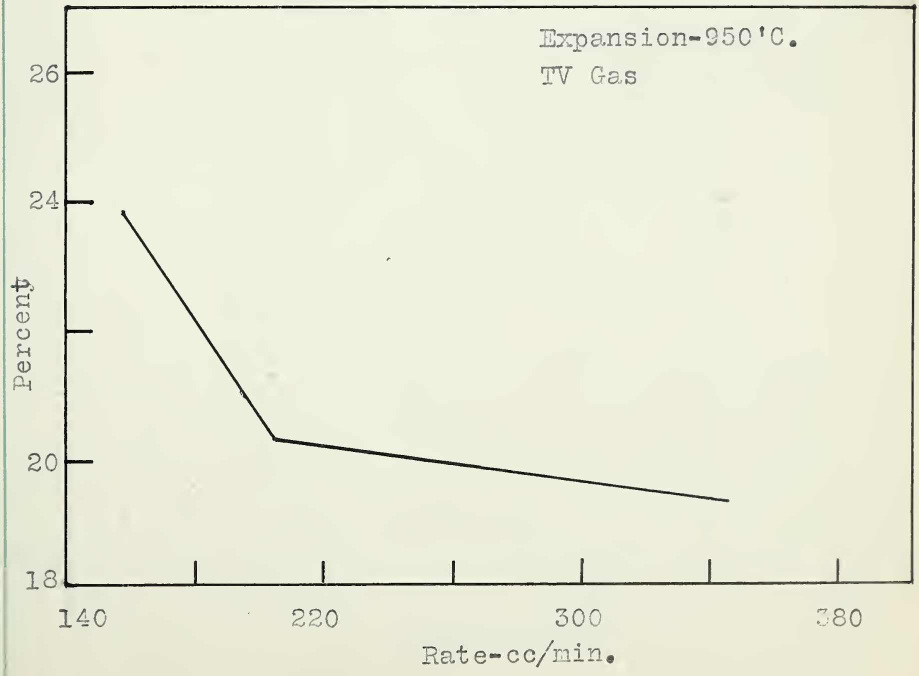

Expansion-950'C.
TV Gas
Percent
26
24
20
18
140
220
300
380
Rate-cc/min.

Fig.49

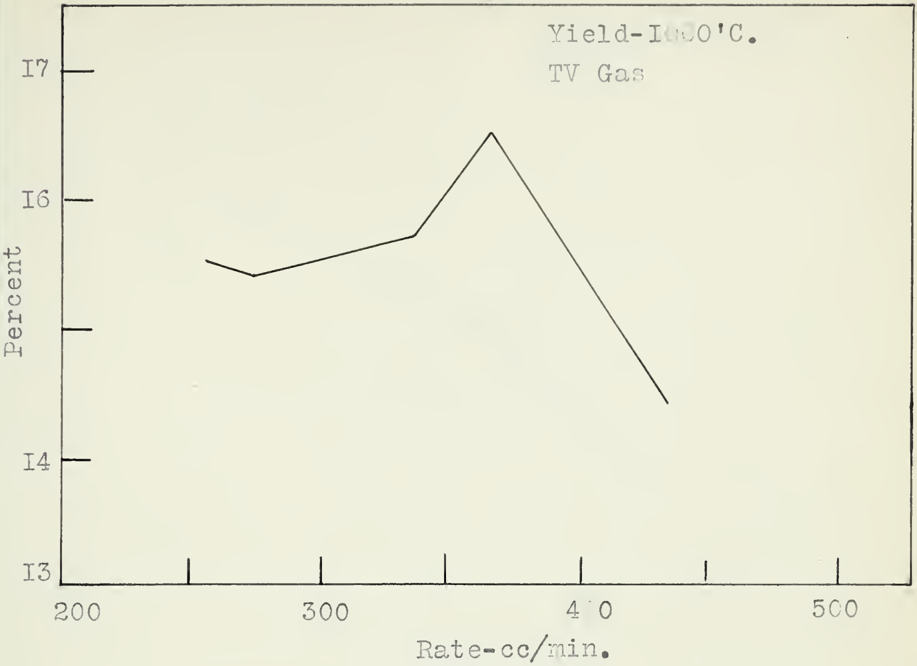

Yield-I000'C.
TV Gas
I7
I6
I4
I3
Percent
200
300
400
500
Rate-cc/min.

Fig50

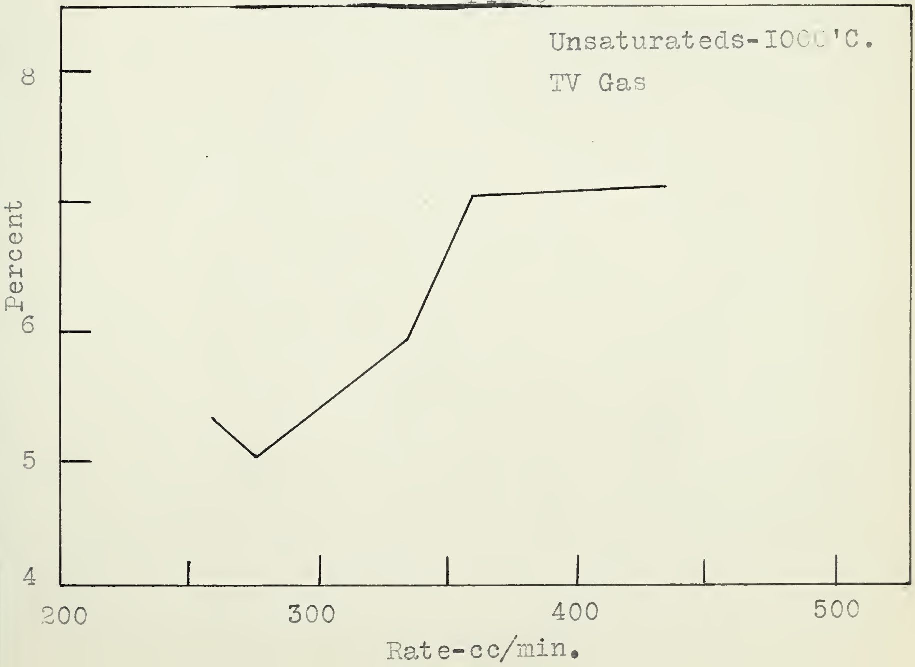

Unsaturateds-I000'C.
TV Gas
8
6
5
4
Percent
200
300
400
500
Rate-cc/min.

Fig.5I

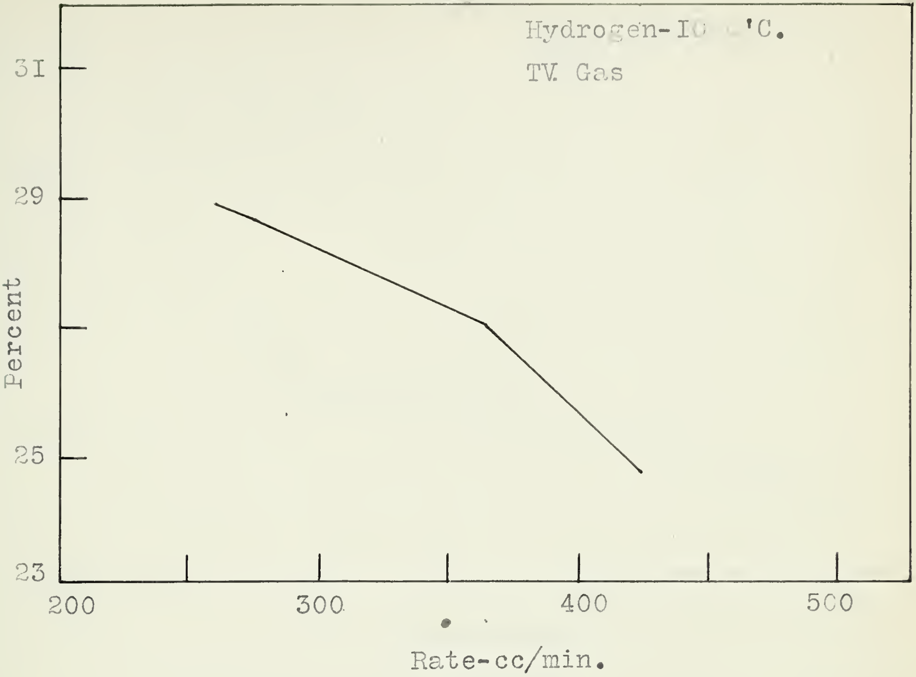

Hydrogen-IO[illegible]'C.
TV. Gas
Percent
3I
29
25
23
200
300
400
500
Rate-cc/min.

Fig.53

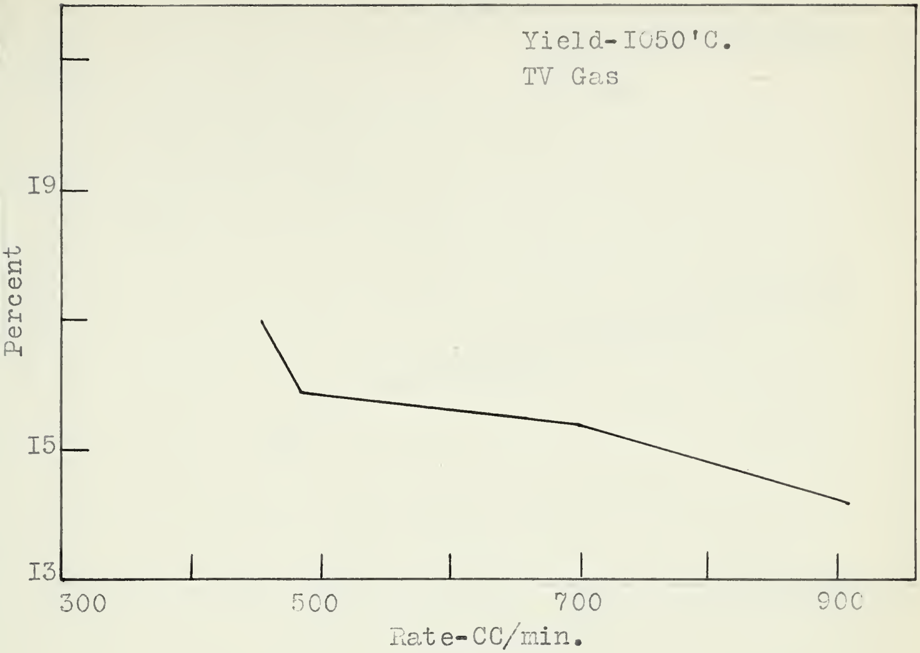

Yield-I050'C.
TV Gas
Percent
I9
I5
I3
300
500
700
900
Rate-CC/min.

Fig.54

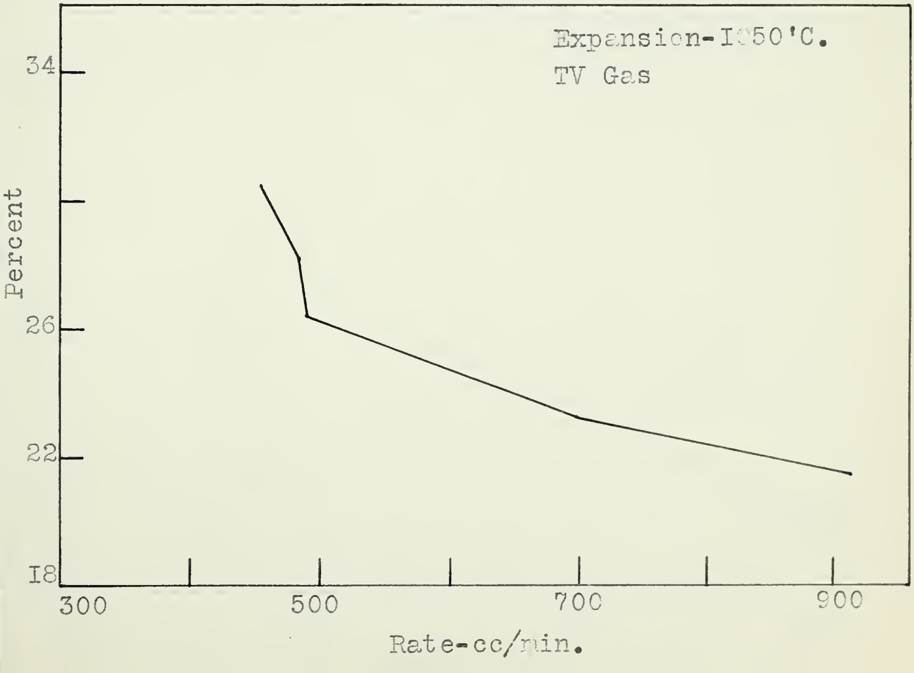

Expansion-I050'C.
TV Gas
Percent
34
26
22
I8
300
500
700
900
Rate-cc/min.

Fig. 55

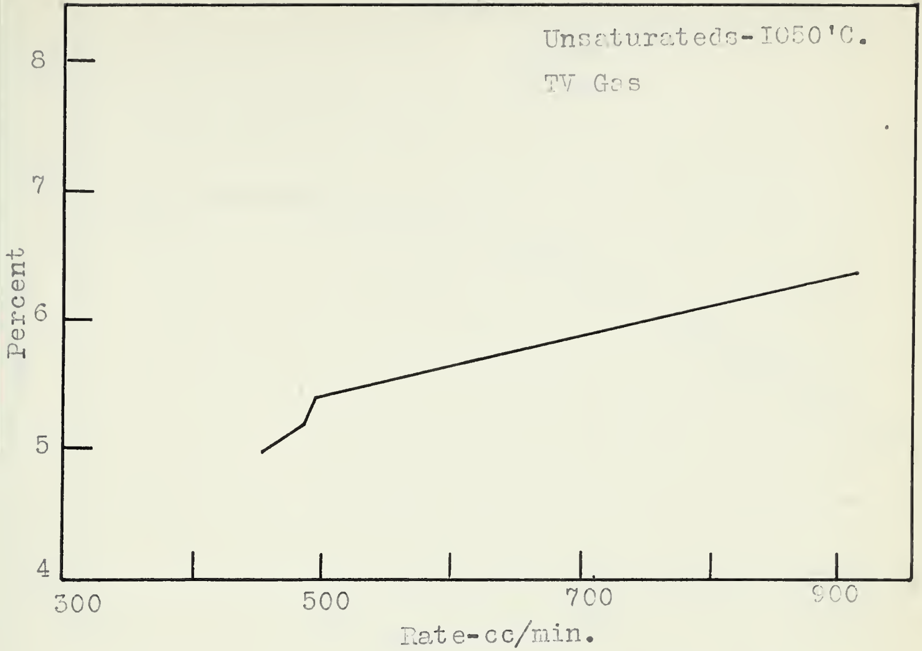

Unsaturateds-I050'C.
TV Gas
Percent
8
7
6
5
4
300
500
700
900
Rate-cc/min.

Fig.56

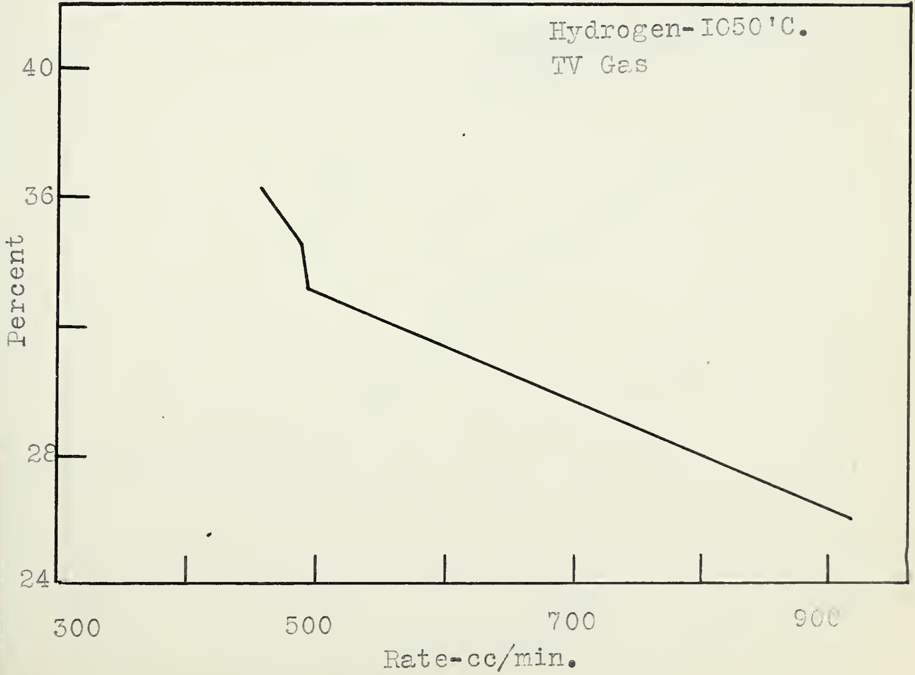

Hydrogen-I050'C.
TV Gas
Percent
40
36
28
24
300
500
700
900
Rate-cc/min.

Fig.57

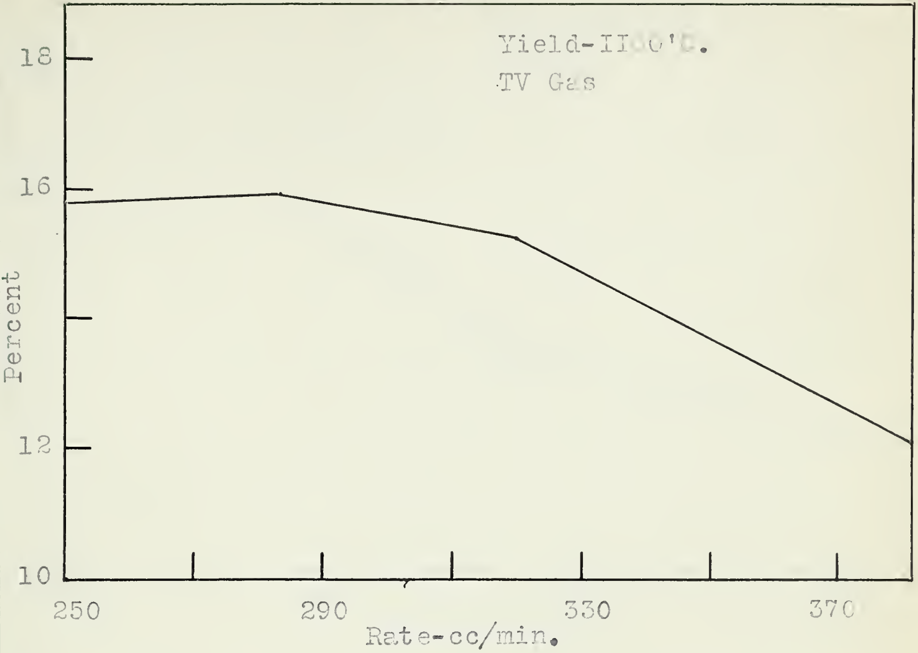

Yield-1100'C.
TV Gas
18
16
12
10
Percent
250
290
330
370
Rate-cc/min.

Fig.58

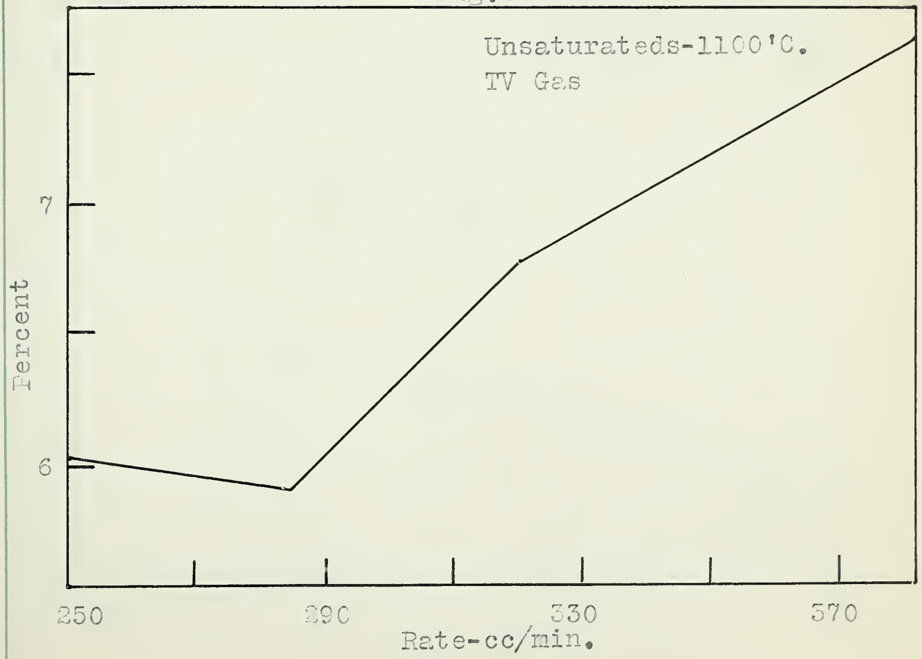

Unsaturateds-1100'C.
TV Gas
7
6
Percent
250
290
330
370
Rate-cc/min.

Fig.59

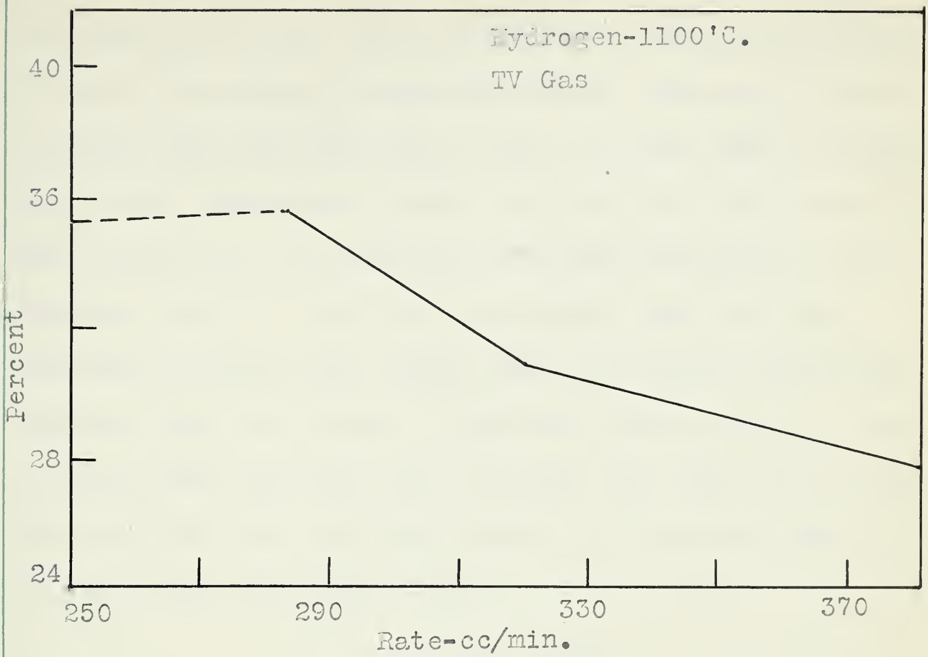
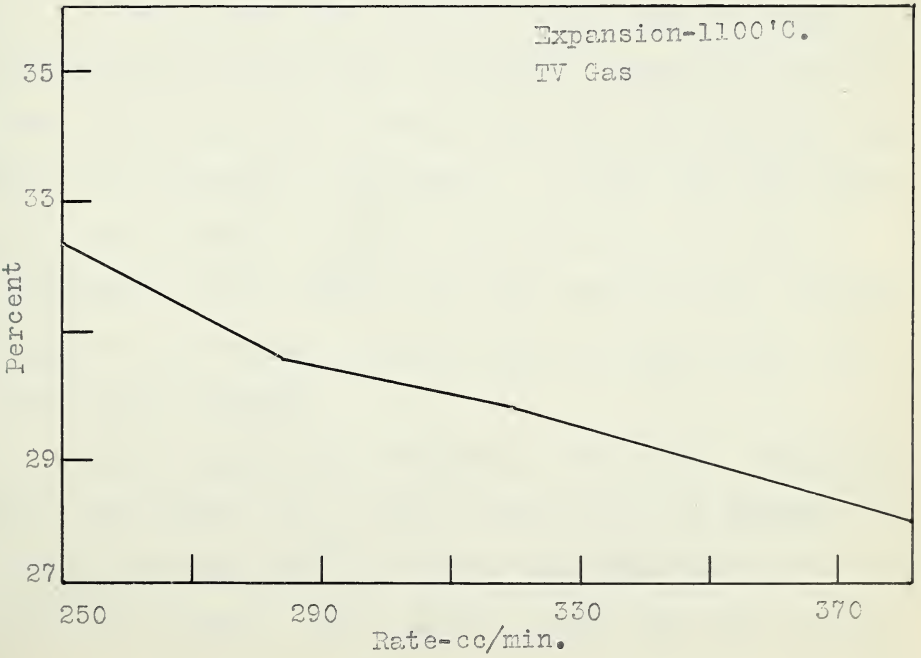

Hydrogen-1100'C.
TV Gas
40
36
28
24
Percent
250
290
330
370
Rate-cc/min.

Fig.60


Expansion-1100'C.
TV Gas
35
33
29
27
Percent
250
290
330
370
Rate-cc/min.

It can be seen in run #200 that as the gas rate increases the total yield decreases. It is interesting to note the effect of gas rate on the tar/light oil ratio. In step (a), tar/light oil = 1.6. As the rate increases this ratio diminishes, until in step (d) it is 0.6. This same effect can be noted in runs #198 and #199. If a maximum yield of light oil is sought, this will be obtained at some rate higher than that which gives the maximum total oil yield. Comparing #200 a and d it can be seen that the total oil in grams per cubic foot drops from 2.58 to 2.20, but the light oil increases from 1.00 to 1.37 grams per cubic foot.

2. 7-mm. Tube

It was found that with a 1.5 cm. tube at temperatures of 1100, and particularly at 1150°C., that the apparatus used in the previous section could not efficiently cope with the necessary high rates. A 7 mm. tube was therefore substituted. It was found difficult to make a successful run at 1150°C. as the reaction tube rapidly plugged with carbon, even at rates in which white oil fumes were produced.

Table X gives the results of this work. Comparing this with Table IX, it can be seen that the maximum oil yield occurs at 1050°C. Above this temperature the yield falls off slowly. It is worth noting that with Viking

gas, the yield gradually increased as the temperature was raised, and the maximum yield was obtained at 1150°C. Hague and Wheeler state that methane is considerably more stable than higher saturated hydrocarbons. Temperatures of 1100°C. or greater, appear to be higher than will produce oil from aliphatic hydrocarbons such as ethane, propane and butane. As the temperature increases above 1050°C. the tar/light oil ratio rapidly increases. In run #201-1, with the temperature at 1100°C., the tar/light oil ratio is 2.4, and in step 4 it is 1.7. The reaction gas was in the furnace 3.80 and 2.46 seconds respectively. In run #202, at 1150°C., the tar/light oil ratio for maximum yield is 5.4. At a higher rate this drops to 2.3. The reaction gas was in the furnace 2.3 and 1.8 seconds respectively.

The highest yield obtained from Turner Valley gas by pyrolysis in one step was 0.7 gallons per 1000 cu. feet, as determined by weight increase. This yield was obtained at 1050°C.

3. Circulation Experiments

A study of the pyrolysis of Turner Valley gas in stages was carried out. An attempt was made to determine the maximum amount of oil obtained by this method. Two procedures were followed: in the first experiment the

TABLE X

TURNER VALLEY GAS

Run	Temp.	Vol.	Rate	Time in Furnace	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Total Oil	Yield	Yield
#	°C.	Cu.Ft.	cc/min.	Sec.	%	%	%	%	Grms.	Grms.	Grms.	%	Gal./ 1000 c.ft.
201-1	1100	1	248	3.80	32.3	6.2	35.3	-	1.90	.74	2.64	15.9	0.65
2			283	3.33	30.6	6.1	35.6	53.8	1.89	0.78	2.67	16.0	0.65
3			320	2.94	29.8	6.8	31.1	57.2	1.60	0.75	2.35	15.3	0.62
4			383	2.46	28.0	7.5	27.8	59.8	1.26	0.74	2.00	12.1	0.49
202-1	1150	1	412	2.30	32.4	7.3	33.6	-	1.74	0.32	2.06	12.4	0.51
2			490	1.92	-	7.1	34.0	-	1.21	0.50	1.71	10.4	0.42
3			517	1.83	33.2	8.0	30.0	-	1.18	0.52	1.70	10.4	0.42

gas was subjected to one comparatively gentle heat treatment, followed by three more intense treatments; and in the second experiment the gas was given intense heat treatments in all four steps. Each experiment will be described in turn.

In run #196, furnace 1 was maintained at 900°C. and the gas flow adjusted to yield just a trace of fog. The tar settling in the trap was more fluid than usual, and was dark brown instead of the usual black color. The total yield, by weight increase, amounted to 8.7%. Furnace #2 was maintained at 1000°C. The fumes were a dense rich cream, and a yield of 10.4% by weight increase was obtained. The temperature of the third furnace was also maintained at 1000°C., but the rate was lowered to yield dense fumes. The yield was 7.9%. In the fourth furnace the temperature was raised to yield the largest amount of oil possible. The necessary temperature was found to be 1080°C. The fumes still appeared quite dense, but the yield dropped to 6.0%. The light oil was steamed from the charcoal absorbers. The total amount of oil recovered was 1.16 gallons per 1000 cu. feet, and consisted of 0.43 gallons tar, and 0.73 gallon light oil. The yield as determined by weight increase amounted to 1.33 gallons per 1000 cubic feet.

In run #197 the first furnace was maintained at

TABLE XI

CIRCULATION EXPERIMENTS - TURNER VALLEY GAS

Run	Temp.	Vol.	Rate	Time in Furnace	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Total	Yield	Yield
#	°C.	Litres	cc./mm.	Secs.	%	%	%	%	Grms.	Grms.	Grms.	%	Gal./1000 c.ft.
196-1	900	228	169	10.2	14.8	7.2	15.7	73.5	2.38	9.09	11.47	8.7	0.35
2	1000	"	193	8.9	5.0	4.0	27.8	60.2	5.23	8.45	13.68	10.4	0.42
3	1000	"	140	12.3	5.2	3.4	34.5	57.0	3.72	6.87	10.59	7.9	0.32
4	1080	"	147	11.7	4.7	2.9	42.4	40.7	2.92	5.05	7.97	6.0	0.24
							Totals		14.25	29.46	43.71	33.0	1.33

Recovery = 1.16 gal./1000 cubic feet.

Run	Temp.	Vol.	Rate	Time in Furnace	Expansion	Unsaturateds	H_2	CH_4	Tar	Light Oil	Total	Yield	Yield
197-1	1000	215	286	6.0	21.9	7.1	24.6	65.7	7.55	12.15	19.70	15.6	0.64
2	1070	"	349	4.9	6.9	4.3	41.5	50.0	6.35	5.85	12.20	9.7	0.39
3	1000	"	170	10.1	2.0	3.3	43.9	47.2	3.35	6.77	10.12	8.0	0.33
4	1070	"	174	9.9	3.7	2.6	49.1	44.7	2.24	5.74	7.98	6.3	0.26
							Totals		19.49	30.51	50.00	39.6	1.62

Recovery = 1.4 gal./1000 cu. feet.

1000°C., and the rate adjusted to give as high a yield of oil as possible. A yield of 15.6% was obtained. In each of the three following steps the yield was 9.7, 8.0 and 6.3% respectively. The total yield by weight increase amounted to 39.6%, or 1.62 gallons per 1000 cubic feet.

The total oil recovered was 1.4 gallons per 1000 cubic feet. Of this there were 0.775 gallons light oil and 0.625 gallons tar. This represents the highest yield obtained from Turner Valley gas.

It is interesting to note that in run #197 the percentage tar is higher than that obtained in #196. However, the amount of light oil recovered in #197 is slightly greater than in #196. A more detailed study of the above is given in Table XI, P. 112.

C - Analysis of Products

During the first part of the work the light oil and tar products were collected separately, until sufficient had accumulated for fractionation. In some of the later experiments sufficient light oil was produced in a single run for individual fractionation on a micro column as described by Cooper and Tasce (7).

The light oil removed from the charcoal was usually golden yellow in color. This color was found due to

small amounts of tar which had passed through the electrical precipitator. In experiments in which the precipitator was working efficiently, the light oil obtained had very little color. The odor of benzene was masked by that of toluene and the xylenes.

On fractionation, 150 cc. of light oil produced from Viking gas yielded the following:

I.B.P.	75°C.	(uncorrected)	
81%	80.5°C.	probably	benzene
91.4%	112°C	"	toluene
93.4%	150°C.	"	xylenes
10 cc.	residue	"	naphthalene

The residue had a boiling point of 180°C. and did not decompose up to 200°C. On cooling, naphthalene crystallized out. The distillates were water white. They were placed in stoppered flasks and after four months showed no traces of color.

The light oil produced from the Turner Valley gas was found to be similar to that from Viking gas. An analysis of the Turner Valley product as performed on the micro fractionating apparatus is given below.

Volume used = 24 cc.

I. B. P.	33°C.
10.2%	77°C.
51.8%	78°C.
72.7%	81.5°C.
83.3%	92°C.

The distillation was discontinued at 92°C. Approximately 75% of the oil is benzene. There are traces of lower boiling substances, and 10 to 15% toluene.

A collection of tar from several experiments, weighing 51.3 grams, was distilled, yielding the following:

I. B. P.	79°C.
1.8%	100°C.
3.5%	210°C.
12.3%	218°C.
17.5%	235°C.
22.8%	245°C.
31.6%	290°C.
44%	345°C.

The distillate up to 245°C. was a pale yellow oil which solidified on cooling. It contained naphthalene and a wax-like substance. 2.7 grams of a quite fluid brown oil distilled over between 245-290°C. 6.2 grams distilled over between 290-345°C. This was a solid at room temperature, and contained anthracene. Above 345°C. an orange colored waxy substance was obtained. The residue was a solid black glossy pitch.

The limited quantity of tar prevented a detailed analysis, however distillation of the tar showed it to have a boiling range somewhat similar to that of coal tar. It contained no acids or bases.

Several substances were identified:

1. Naphthalene - the distillate coming over between 180 and 220°C. was largely naphthalene.
2. Anthracene - the 290-345°C. fraction partly sublimed to form characteristic purple anthracene crystals.

3. Chrysogene - part of the pitch was ground into a powder and a small amount was extracted with benzene. The residue was extracted with petroleum ether. The petroleum ether solution, on evaporation, yielded orange yellow chrysogene crystals.

4. Chrysene - the above crystals were tested for chrysene by adding concentrated sulfuric acid. The resulting purple solution indicated the presence of chrysene.

5. Diphenyl methane - a substance distilled over in the 240-280°C. range which had a melting point between 25-30°C. This was identified as diphenyl methane. The fraction was treated with sulfuric acid. An oil layer separated out which at -15°C. solidified.

V - DISCUSSION

Before considering the reaction mechanism responsible for the observed results, a summary of the salient points is in place. The two products, oil and gas, and their relation to the two variables, temperature and rate of flow, will be considered. It is not possible to consider the geometry of the reaction tubes at present. The dimensions do not appear to exert an appreciable influence when compared to the effect of temperature.

As might be expected, the hydrogen production and the percentage expansion increase as the temperature is raised or as the rate of flow is decreased. The methane surviving the reaction follows the exact reverse of this behavior.

The oil yields have been found to increase with increase in temperature and decrease with increasing rate of flow. Turner Valley gas yields a greater quantity of oil than does Viking gas, which is to be expected in view of the larger amount of higher hydrocarbons in the former. The yield in both cases can be increased greatly, twice or more, by pyrolysis in steps. This procedure results in the production of a larger amount of light oil than is possible in one step under optimum conditions. The presence of hydrogen is probably responsible for this behavior. Hague and Wheeler (15) assumed that the surface

of the graphitic carbon formed in the reaction tube becomes covered with a thin layer of hydrogen due to the reaction $CH_4 \longrightarrow C + 2H_2$ which takes place readily on surfaces. This hydrogen layer prevents the further decomposition of methane in the above manner. The work under discussion bears out this assumption.

As would be expected, the production of carbon and of tar decreases as the hydrogen content of the gas increases. The protective action of the hydrogen in allowing less methane to reach the walls would play its part. Moreover, all reactions leading to carbon or tar liberate hydrogen and the presence of excess hydrogen would retard such reactions.

It was found that within limits, the relative amounts of tar and light oil products could be controlled. The relative amounts of tar and light oil follow definite courses. For short heat treatments and low temperatures the light oil fraction increases and for long heat treatments and high temperatures the tar fraction increases. The conditions of maximum total yields do not represent conditions of maximum light oil yields. Invariably the temperature is too high or the rate too low. The conditions producing large tar yields also lead to the greatest decomposition to carbon and hydrogen. Turner

Valley gas was found more sensitive in this respect than Viking gas. With Turner Valley gas, temperatures above 1050°C. produced excessive amounts of tar, even at relatively high gas rates. Tar formation was reduced by using low temperatures and high gas rates. This, however, reduced the total yield. It was found possible to obtain high yields and still keep the tar fraction at a minimum by the use of hydrogen.

If it is light oil which is sought, it is believed that the best method of obtaining it is by pyrolysis in steps. With Turner Valley gas the first furnace should be at a temperature between 900 and 1000°C. and the rate should be so adjusted to yield a faint white fume. It is believed that the higher hydrocarbons which are not nearly so stable as methane will under these conditions decompose to yield a maximum amount of oil. It was found that at 900°C. with a relatively high rate of flow no hydrocarbons above methane remained undecomposed. This first gentle heat treatment also produced sufficient hydrogen to prevent excessive tar formation on further more intense heat treatment. The yield obtained by this method was 1.16 gallons per 1000 cu. feet. Of this 0.73 gallons were tar and 0.43 gallons were light oil. With more severe heat treatment in the first step the yield was 1.4 gallons per 1000 cu. feet of recovered oil. Of

this there were 0.625 gallons tar and 0.775 gallons light oil.

The absence of ethane or any higher saturated hydrocarbons in the exit gases under all conditions used with Viking gas or Turner Valley gas is to be noted.

The production of unsaturated gaseous hydrocarbons is of importance. The total amount of such increases with rate of flow in a regular manner at any constant temperature. At constant rate of flow and increasing temperature, they appear to remain constant or decrease slightly. However, under conditions of good oil yield; that is, increasing rate of flow with increasing temperature, the production of unsaturated hydrocarbons increases. In regard to the individuals, acetylene and ethylene, they follow in general the above rules and appear to parallel one another. Exceptions have been noted in the case of acetylene at 950°C. Here the acetylene appears to pass through a maximum as the rate of flow increases.

This behavior of the total unsaturateds is the reverse of that found for the yield of oil. At a given temperature the oil production increases as the rate is decreased. It is probable that the oil yield would ultimately decrease with decreasing rate, but such conditions were not experienced. The production of carbon

increased rapidly at low rates of flow, and the reaction tube was plugged in a short time, thus limiting the range available for experiment.

Stanley and Nash (26) find that ethylene and acetylene follow the yield of oil very closely. This is the reverse of the present findings; that increasing oil yield occurs with decreasing ethylene and acetylene yields. No explanation of the discrepancy can be offered.

The production of unsaturated compounds with Turner Valley gas is generally twice as great or more than in the case with Viking gas. Only two determinations have been made of acetylene produced by the pyrolysis of Turner Valley gas and they followed the same rule.

At 950°C. and 11 seconds in the furnace, the acetylene production was 0.69%, and at 1000°C. and 7 secs. in the furnace, the acetylene production was 1.00%.

The recirculation experiments yield interesting results on the unsaturated hydrocarbons. With Viking gas the total unsaturated percentage does not change appreciably on successive pyrolysis. With Turner Valley gas the initial high value of 7% or so is reduced with each succeeding passage, until it is the same or slightly less than in the case with Viking gas, about 3%. This behavior might be predicted in view of the similar nature of the two gases after the first passage. No saturated hydrocarbon other than methane survives. The material

undergoing pyrolysis is nearly the same in each case and the same ultimate production of ethylene and acetylene would be expected.

The accepted mechanisms for the reactions during pyrolysis of simple hydrocarbons due to Stanley and Nash (26) and Wheeler and Wood (29) have been discussed previously. Essentially they assume the existence of unstable CH_3, CH_2 and CH groups which can be rearranged to form the various products found. It is proposed here that a simpler mechanism will suffice to account for all the products and is more in line with the experimental evidence. In brief, it is only necessary to assume the existence of CH_2 groups to account for the observed facts. The mechanism is similar in its results to the proposals of Hague and Wheeler (15) who show that ethylene is sufficient to account for all the products.

The assumption of the existence of CH_3 residues is not improbable, but is unnecessary. These residues are supposed to combine with the formation of ethane which in turn is dehydrogenated to ethylene. At temperatures as low as 900°C. no ethane has been found in the products. Should ethane be formed in the reaction, it is probable that traces would survive. Therefore there is no evidence for the formation of CH_3, at least in

appreciable amounts, and moreover, there is no necessity for its occurrence.

Ethane does not yield aromatic hydrocarbons directly (Hague and Wheeler (15a), but first produces ethylene. The ethylene produced from ethane by dehydrogenation would be the source of CH_2 residues, and has been shown sufficient to produce aromatic hydrocarbons. (15).

The occurrence of acetylene would lend support to the formation of CH groups and acetylene will quite readily produce the aromatic hydrocarbons formed. Apart from the improbability of the existence of such an unstable group as CH, the evidence suggests that the acetylene formed is derived from ethylene. On pyrolysis ethylene readily yields acetylene and that this is the source of the acetylene in question is supported by the obvious parallelism between ethylene and acetylene in the gas produced.

The following simple primary reactions are proposed, of which the production of C and H_2 and acetylene occur only to a slight extent.

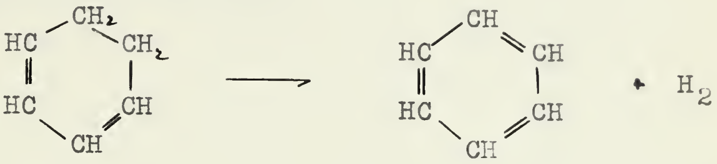
$$\begin{tikzcd} C + H_2 & 2CH_4 \arrow[l] \arrow[r] & 2{:}CH_2 + H_2 \arrow[d] \\ & C_2H_2 \arrow[d] & C_2H_4 \arrow[l] \arrow[dl] \\ & \text{Aromatic Hydrocarbons.} & \end{tikzcd}$$

Ethylene may be assumed to follow the mechanism of Hague and Wheeler (15) to yield aromatic hydrocarbons.

A simplified mechanism differing only in discarding certain intermediate fugitive compounds is as follows:

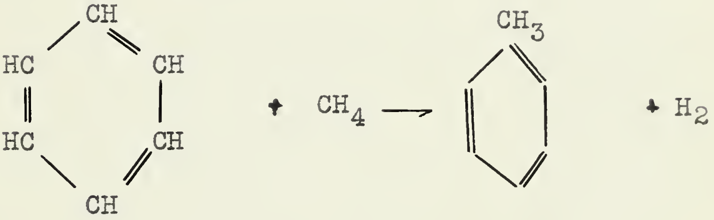
$$2\ C_2H_4 \longrightarrow CH_2:CH\cdot CH:CH_2 + H_2$$

$$CH_2:CH\cdot CH:CH_2 + CH_2:CH_2 \longrightarrow CH_2:CH\cdot CH:CH\cdot CH:CH_2 + H_2$$

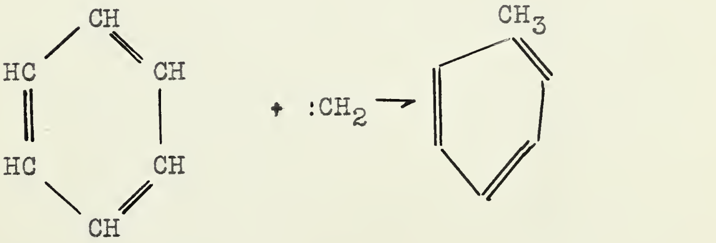


The formation of toluene may be explained in two ways:

1.



2.



In the second case one hydrogen of the benzene ring migrates to the carbon of the side chain.

Polycyclic compounds, such as naphthalene, may be assumed to be formed by the addition of a benzene and a butadiene molecule with the subsequent splitting off of 2 hydrogen molecules.

VI - SUMMARY

Viking and Turner Valley gas have been studied between the temperatures of 900 and 1150°C. The oil and gas products at various gas rates have been determined both qualitatively and quantitatively. The factors influencing the nature of the products and methods of obtaining these products have been stated. The influence of the walls of the reaction tubes and also of inert gases such as hydrogen have been described. The maximum yield of oil recovered has been stated. It is as follows:

1. For a single heat treatment Viking gas yielded 0.43 gallons per 1000 cubic feet. Of this 0.22 gallons were light oil and 0.21 gallons were tar. Turner Valley gas yielded 0.66 gallons per 1000 cubic feet. Of this 0.36 gallons were light oil and 0.30 gallons were tar.

2. For four heat treatments of the same gas, Viking gas yielded 0.92 gallons per 1000 cubic feet. Of this 0.47 gallons were light oil and 0.45 gallons were tar. Turner Valley gas yielded 1.4 gallons per 1000 cubic feet, of this 0.775 gallons were light oil and 0.625 gallons were tar.

The percentage conversion of methane to oil has been found to be approximately 45%. This percentage conversion was found to increase and to approach 100% with increasing concentration of hydrogen. The amount of methane decomposed in a single heat treatment was found to amount to from 15 to 30%, depending on the severity of the treatment. The amount of hydrogen produced was found to vary from 12 to 35%, and the unsaturated hydrocarbons formed varied from 2.5 to 7%. The gas expansion varied from 5 to 25%. The residual gas was found to be a good fuel gas. It had a lower ignition temperature and burned faster than the original gas due to the unsaturated hydrocarbons and hydrogen present.

A mechanism has been proposed and discussed.

In concluding, the writer wishes to take this opportunity to thank Dr. E. H. Boomer under whose direction this work was carried out, for all the kindly advice and valuable time he so generously devoted to the work. The writer is greatly indebted to the Research Council of Alberta, and the National Research Council for their financial aid. He wishes to thank the members of the Chemistry Department for their many valuable suggestions. The assistance of Mr. A. T. Baker in the preparation of this paper is gratefully acknowledged.

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